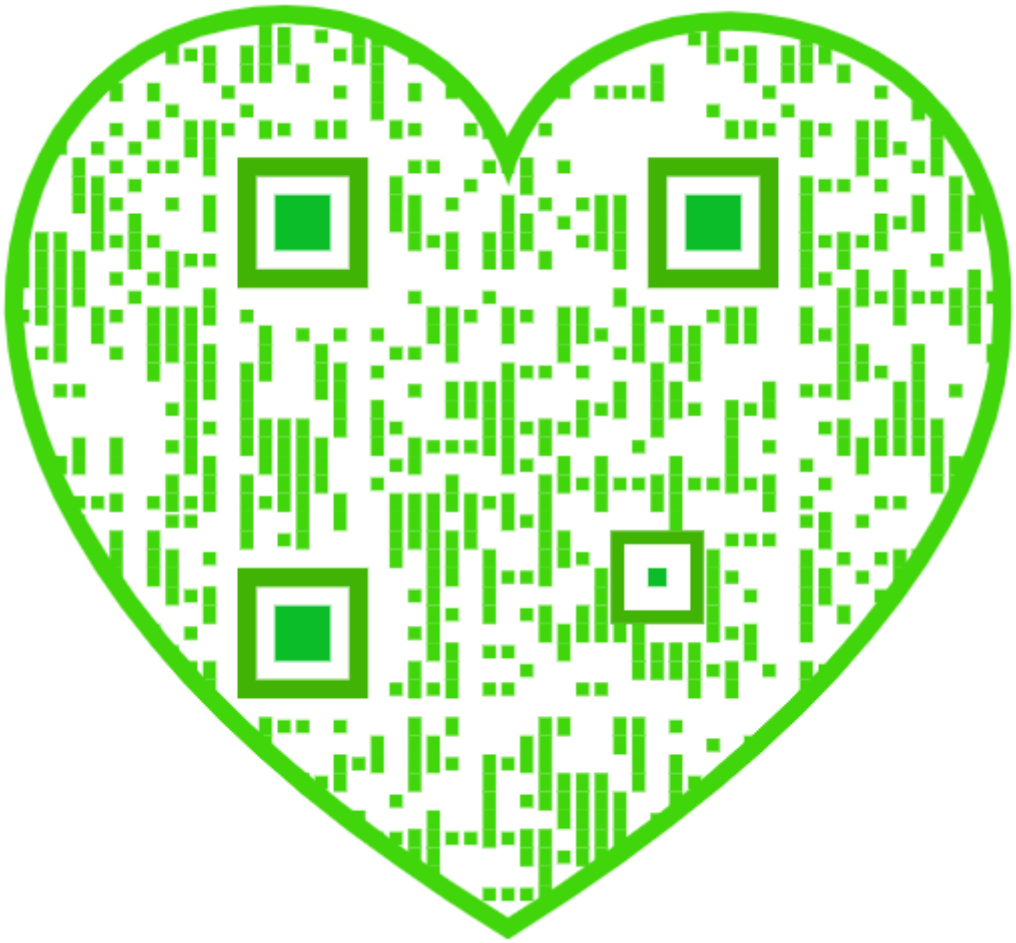

COAL-TAR AND AMMONIA.

BEING THE SECOND AND ENLARGED EDITION

OF

'A TREATISE ON THE DISTILLATION OF COAL-TAR AND AMMONIACAL LIQUOR.'

BY

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PREFACE.

When the first English edition of this treatise, which appeared in 1882, was approaching exhaustion and a new edition had to be prepared, I did not think it suitable to simply reprint the book, with such additions as would be indispensable, but I preferred remodelling it to a great extent. In the first place, a very large amount of matter pertaining to the subject has been published in the interval, consisting mostly of patent specifications and of papers appearing in scientific periodicals; and all this had to be incorporated with my treatise. But over and above this, since the issue of the former edition my own personal experience in this line has been extended; and I have been enabled to make considerable additions to nearly all parts of the work, owing to the kindness of several owners and managers of tar- and ammonia-works, who allowed me to minutely inspect their factories, and supplied me with a great deal of special information, extremely useful for practical purposes. My thanks in this respect are principally due to Dr. Grüneberg, of Cologne, Dr. Wanstrat and Mr. Vinckh, of Amsterdam, Mr. Wilton, of the London Gas-Light and Coke Company, and, above all, to Mr. S. B. Boulton, of Messrs. Burt, Boulton, and Haywood, who has moreover made large contributions to the text, which appear in the proper places. From fifteen other gentlemen, practically employed in the manufacture of coal-tar products and ammonia, I have been favoured with information on a large number of points submitted to them;

and Mr. Watson Smith has again taken the trouble of looking over the proofs. This has also been done (after printing) by Dr. Krämer, one of the first continental authorities on tar-distilling; and a number of his suggestions will be found in the "Addenda." I have thus practically enjoyed the collaboration of some of the first men in this trade, and their friendly services are most gratefully acknowledged by me.

It appeared necessary to add several new chapters, embracing the recovery of coal-tar and ammonia from other sources than the manufacture of illuminating-gas, the burning of tar as fuel, and various other matters. Several of the other chapters were completely rewritten. Since, now, the old title—'The Distillation of Coal-Tar and Ammonia'—does not at all cover the whole scope of this present treatise, its title has been altered to 'Coal-Tar and Ammonia.' The work now contains 739 pages of letterpress and 191 diagrams, against 383 pages and 88 diagrams in the first edition; but, apart from this outward extension, there are but few pages in this new edition which have been taken unchanged from the former one, modifications and improvements having taken place all over; so that this is to all intents and purposes a new book. May I be permitted to hope that it will retain the friends which its predecessor has gained, and make some new ones as well. It is a good augury for its appearance that the extreme depression in the value of all tar-products, as depicted in the first chapter (written about a year ago), has now given way to a more healthy state of affairs, and that those labouring in this field need not look with despondence into the future of this important trade.

Zurich, July 1887.

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COAL-TAR AND AMMONIA.

CHAPTER I.

INTRODUCTORY.

The process of destructive distillation of organic substances (that is, of heating them beyond the point of decomposition without access of air) is carried on for several industrial purposes. The principal object may be either the dry residue, or the gases evolved, or else the condensed distillate. The latter nearly always separates into two distinct layers—one of which consists of the water preexisting in the original substance, or formed from it during destructive distillation, holding in solution a portion of the distillate; the other is formed by the condensed products insoluble in water, appearing in the form of a more or less viscid dark-coloured oil, in some cases lighter, in others heavier than the watery distillate, and generally known by the name of *tar*.

According as the original materials differ, the products of their destructive distillation differ also; but the difference is much greater in the condensed distillates than in either the solid residue or the permanent gases. The *solid residue* is always essentially carbon; at least it is usually assumed to be. Hence the different qualities of wood-charcoal, coke, bone-charcoal, &c. are principally caused by the various descriptions and quantities of mineral matter intimately mixed with the carbon remaining behind as the residuum of the organic matter, and varying according to the original substance. Along with this it should not be over-

looked that the process of destructive distillation is industrially carried on at very different temperatures, by which the physical nature of the carbonaceous residue is greatly modified. Probably this plays at least as important a part as the difference between the original materials. But it is also very possible that the molecules of carbon in wood-charcoal, coke, &c. do not consist of the same number of atoms. Lastly, it is certain that in these bodies, besides free carbon, certain compounds of carbon, hydrogen, oxygen, and even nitrogen occur, the isolation or even the recognition of which has not yet been accomplished. In any case it cannot be denied that the *combustible* portion of all carbonaceous residues, so far as the chemical reactions throw light upon it, does not present any great diversity.

The same may be said of the *permanent gases*, not remaining dissolved in the products of condensation, which are formed in destructive distillation. Carbon dioxide, carbon monoxide, nitrogen, hydrogen, the lowest members of the paraffin series, and of the hydrocarbons containing less hydrogen (ethylene, acetylene) are always found. Sulphuretted hydrogen does not occur in the distillation of wood, but occurs regularly in that of coal and of animal matters. The production of these permanent gases for illuminating-purposes is the object of a comparatively recent but highly important industry, in which now more than ever *coal* predominates almost to the exclusion of all other raw materials, except for very special purposes.

On the other hand, the *watery distillates* differ very much according to the nature of the raw material. In the case of wood, which contains very little nitrogen, these products are of an acid nature, acetic acid being the most important, next to which come methylic alcohol and acetone. The products originating from fossil vegetable substances behave in this respect similarly to wood, if they have been formed in the present or the more recent geological periods—for instance, peat and browncoal (lignite). The acid reaction of the distillate is frequently quoted as a criterion for distinguishing browncoal from real coal. All the methylic alcohol and most of the acetic acid of commerce are obtained from this source. Real coal, on the other hand, which always contains a certain amount of nitrogen, invariably furnishes a watery distillate whose reaction is strongly alkaline, owing to the presence of ammonia and, to some extent, of volatile organic bases. The bulk

of ammonia and ammonia-salts comes from this source, viz. the ammoniacal liquor of gas-works, which is obtained not merely by simple air-condensation, but also by direct washing of the gas in the scrubbers.

A similar difference exists in the oily distillates, the *tars*. We may say, generally, that the tar from peat, browncoal, and bituminous shale consists *principally* of hydrocarbons of the "fatty" series, wood-tar of phenols and their derivatives, and coal-tar of "aromatic" hydrocarbons. But along with the principal constituents there is always a large number of other compounds present; and matters are still further complicated by the fact that through the action of heat the individual compounds are transformed partly into other compounds of the same series, partly into compounds belonging to other series. Owing to this, tar obtained from the same material differs very much in composition according to the temperature of the dry distillation—nay, even according to the shape of the retorts, which allows the vapours to remain for a greater or less time in contact with the hot sides of the vessel.

This explains why the tars are extremely complex mixtures, whose unravelling has not been anything like completely accomplished even in the best-known case, that of coal-tar, much less in the other cases, owing to the extreme difficulties connected with this kind of research. It is true that acids (phenols) and bases can be separated at least by "serial reactions;" but the great bulk of indifferent hydrocarbons can only be separated from one another by fractional distillation, only a few of them by crystallization or by the formation of sulphonic acids, &c. Of these operations the first is often insufficient for isolating the simple compounds, especially those of high boiling-points, since at the boiling-temperature the compounds are frequently decomposed.

Browncoal-tar, as well as that obtained from peat and bituminous shale (and formerly also from the Torbane-Hill mineral), is manufactured for its own sake as a principal product, and forms the basis of the West-European industry of mineral oils and paraffin, which has proved its vitality even against the enormous competition of American and Russian petroleum, of ozokerite, and of other products ready formed in nature. The other products of the destructive distillation of similar more recent fossil substances possess very little or no value, except in the case of some very dense, coal-like browncoals, which furnish good coke and good gas, but no mineral

oil. On the contrary, *coal-tar* has up to the present been nowhere manufactured as a principal product, the other products playing an inferior part; it is only an accidental but unavoidable by-product of the manufacture of lighting-gas from coals, just as ammoniacal gas-liquor is. It is imperative to condense these two substances in order to purify the gas; but whilst the coke remaining behind in gas-making was always a by-product of considerable value, which materially influenced the cost price of the gas, tar and ammoniacal liquor were for many years regarded as refuse products which were not merely without value, but caused considerable inconvenience and expense for their removal. But since during the last quarter of a century coal-tar and ammoniacal liquor have become starting-points for a chemical industry of enormous extent, they have also become factors contributing very greatly to the revenue of gas-works; and it can hardly be denied that circumstances might occur in which these two substances would be the principal products of the dry distillation of coal, so that the gas would only appear as a secondary product. It is of historical interest that the first English patent referring to the destructive distillation of coal (that of John Joachun (*sic*) Becher and Henry Serle, dated August 19, 1681) does not treat of the manufacture of lighting-gas, but of "a new way of makeing pitch, and tarre out of pit coale, never before found out or vsed by any other."

We shall see further on that during the last few years the production of tar and ammonia as principal objects of the distillation of coal has been the subject of trials carried out on a large scale.

The proportion in which the by-products of gas-making contribute to the income of gas-works has undergone considerable changes. On the whole, apart from temporary fluctuations, the value of tar and ammonia had been continually rising since the discovery of artificial colouring-matters on the one hand, and the extraordinary extension of beetroot-sugar making (requiring sulphate of ammonia as manure) on the other, had enormously stimulated the demand for these two raw materials. A few years ago, according to a report of the Directors of the South Metropolitan Gas Company, the sale of tar and sulphate of ammonia realized the sum of 9*s.* 5½*d.* per ton of coal distilled. Since the price of coal was 11*s.* 9*d.* per ton, the value of the by-products of gas-making amounted to 82 per cent. of that of the coal employed.

From a private, but trustworthy, source the author can quote the following prices obtained for tar and tar-products about that time:—

Coal-tar in 1883 at gas-works, 55*s.*; at tar-works, 61*s.* to 63*s.*
„ 1884 „ 35*s.*

Pitch, 33*s.* to 35*s.* per ton.

Benzol, 50 to 90 per cent., 3*s.* to 3*s.* 1*d.* per gallon (with cask).

Crude carbolic acid, 1*s.* 8*d.* to 1*s.* 9*d.* per gallon.

Light oil (redistilled), sp. grav. 0·967, 7*d.* per gallon.

Crude naphtha, yielding 50 per cent. at 170° C., 1*s.* 4*d.* per gallon.

Fluid heavy oil, 2¼*d.* to 3¼*d.* per gallon in bulk.

Sulphate of ammonia, good grey, 24 per cent., £14 10*s.* in bags (had been as much as £20 a few years ago).

According to other sources the price of 90-per-cent. benzol in 1883 was 14*s.* per gallon (no doubt only during a short time).

In 1885, however, the price of coal-tar had fallen to about 12*s.*; during 1886 (in England) it was about 7*s.* per ton, and that of 90-per-cent. benzol 1*s.* 8*d.* per gallon. This decline shows no sign of abatement. In Germany coke-oven tar in May 1886 sold at 23*s.* per ton.

The cause of this sudden and violent depreciation of the value of coal-tar (ammonia will be treated of in that respect in the 12th Chapter) is not quite clear. It is true that the great fall in the price of aniline-colours and alizarin, which took place about the same time, and which was undoubtedly owing to over-production, must have influenced the value of coal-tar; but that will not account for the enormous depreciation. Much stress has also been laid on the fact that during the last few years the most strenuous efforts have been made to obtain tar and ammonia from coke-ovens, blast-furnaces, gas-producers, and so forth. But the quantity of tar, of a quality similar to that of gas-tar, which has been actually obtained in Great Britain up to this time, must be only a small fraction of that produced at the gas-works; as we shall see further on, the blast-furnace tar and the Jameson tar cannot at all compete with gas-tar, and the producer-tar can hardly be said to be an article of commerce at the present time.

It seems most probable that the continually increasing production of gas, and consequently of gas-tar, has led to the production of the latter article outstripping the present demand; and

in that case even the comparatively slight addition to the production of coal-tar from coke-ovens must have had a very grave effect on the price of tar. It is a well-known fact that if the supply of a certain commodity continuously, even if but slightly, exceeds the demand, its price is depreciated far out of proportion to the amount of surplus, and the opposite takes place if the demand exceeds the supply. But whilst in most other cases the effect of this is, up to a certain extent, counteracted by the storage of large quantities, both of the raw materials and of the products of manufacture, and by fluctuations in the production of both, it is very different in our case. Gas-tar, on the one hand, must be produced quite irrespective of the demand, since it cannot be avoided in gas-making, and, on the other hand, its storage for any length of time is a practical impossibility. Hence a comparatively slight excess of the supply, which cannot be checked in the way usual with most other raw materials, must soon cause an intolerable glut in the market, and must rapidly force down the price.

It is remarkable that but a short time ago the very opposite fear had become quite general. The apparently enormous strides which the *electric system of lighting* has recently made led to the expectation that the manufacture of coal-gas, and with it the supply of coal-tar, would be greatly reduced. That this is not the case is abundantly proved by what we have just stated.

No doubt the crisis in the coal-tar trade has been aggravated by speculation. A few years ago the prices of tar, benzol, and anthracene were driven up unreasonably by keeping back supplies and storing up immense quantities of benzol and anthracene; and when this "corner" broke down, the reaction, as usual, was all the more severe.

Fortunately there are two directions in which the consumption of coal-tar can be increased to such an extent that better prices may ultimately be obtained again. One of them is the employment of coal-tar, or rather of some of its constituents, for increasing the illuminating-power of coal-gas in lieu of cannel-coal. The other and more immediate and certain way of disposing of a surplus of tar is that of burning it under the retorts. Since the value of tar as fuel, if properly applied (and we shall see, in the 4th Chapter, that this problem is completely solved now), is much superior to that of coke, even if it should not, as has been

asserted, amount to twice as much, it can be most advantageously burned at a time like the present, when coal-tar sells at 7*s*. and coke at 8*s*. per ton.

Let us now take the opposite case, namely, that the demand for the products which have been, up to this time, almost exclusively obtained from coal-tar (that is, practically the great majority of all compounds belonging to the "aromatic series") should be so largely increased that the supply of coal-tar from gas-works would not be sufficient to cover that demand, and that, consequently, the value of coal-tar would be very much increased. Such a state of things, if it ever occurred again, could only be a very temporary one; for more coal than is distilled in gas-works is distilled in *coke-making* for metallurgical purposes; and the problem of obtaining tar and ammonia as by-products in this process, without injuring the quality of the coke, is now satisfactorily solved. It is true, as above stated, that up to the present time the quantity of coal-tar obtained from coke-ovens in Great Britain is not very considerable; but this is partly owing to the fact that the majority of coke-manufacturers have as yet been unwilling to incur the cost of changing their plant, and partly to the fact that some of the efforts made in this country in this direction have been wrongly applied, and may have deterred many others from spending money till it was quite clear which was the best way of attaining the object in view. On the continent it is different; but, strange to say, it is not France (where the first success had been obtained in utilizing the tar and ammonia from coke-ovens), but Germany which has taken the lead in this matter. Within a very short time (in fact since 1882, after the first edition of this treatise had appeared) a very respectable number of coke-ovens, with plant for recovering tar and ammonia, have been put up in Westphalia and other parts of Germany; and it can hardly be doubted that practically all the coke at present manufactured in Germany (which will amount to about one third of that made in Great Britain) would, within a short period, be made in this manner, if the abnormally low price of tar and ammonia did not necessarily put a check upon this change.

During the same time, that is dating from 1882, strenuous efforts have been made to recover tar and ammonia from those *blast-furnaces* which are fed with coals. This industry is principally

limited to Scotland; and we shall see by-and-by what has been done in that respect. The difficulties are here rather greater than in the case of coke-ovens, but they seem to have been overcome in a satisfactory manner.

The recovery of tar and ammonia from *gas-producers* seems a more difficult task, and we shall probably have to wait for a really final solution of that problem till those by-products have again increased in value, so as to make it worth while spending more capital in that direction.

If we further look at the various processes for extracting benzene &c. from ordinary coal-gas, for converting petroleum-residues and other hitherto almost valueless substances into aromatic compounds by the effect of high temperature, and other similar efforts to be mentioned later on, we shall see that there is not the slightest fear of any scarcity of those indispensable raw materials which are the subject of this treatise.

When surveying the manifold sources, not at all, or at least very imperfectly, utilized up till now, from which tar and ammonia can be obtained by means decidedly within our grasp, it would seem useless to speculate, as has been occasionally done, as to what would be the state of affairs if, by processes to be invented hereafter, all the enormous quantities of coals consumed in our households, for raising steam, and for innumerable other purposes (where a recovery of by-products is not at present thought of), should be made to yield up their tar and ammonia as well. It is easy to get out startling figures, say five millions of tons of coal-tar and a million tons of ammonium sulphate for Great Britain alone, but such figures are altogether illusory. They cannot frighten those who are interested in keeping up the price of those materials at a remunerative rate, nor can they offer a solid prospect of benefiting the consumers of those materials, that is, ultimately, the general public; for if ever practicable means should be invented for burning coal in the above-mentioned cases in such a way that the by-products could be collected (perhaps by means of gas-producers), the interest upon the frightful cost of plant and the inevitable working-expenses of collecting the tar and ammonia would, at least in the writer's opinion, in any imaginable case far more than outstrip any profit that might accrue from their sale, taking into consideration the extremely low price which tar and ammonia would command after the opening out of the

more accessible sources of supply from coke-ovens &c., long before the more remote sources just spoken of could come into play.

Historical Notes on the Application of Coal-tar and the Products obtained therefrom.

Before the latter part of the 17th century no notice seems to have been taken of the appearance of tar during the heating of coal—a substance of comparatively small importance at that time. One of the pioneers, if not the real originator, of the industry of coal-tar, the German chemist Johann Joachim Becher, describes his observations in the following words* :—

"In Holland they have peat and in England pit-coals [Steinkohlen]; neither of them is very good for burning, be it in rooms or for smelting. But I have found a way, not merely to burn both kinds into good coal [coke] which not any more smokes nor stinks, but with their flame to smelt equally well as with wood, so that a foot of such coal makes flames 10 feet long. That I have demonstrated with pit-coal at the Hague, and here in England at Mr. Boyle's, also at Windsor on the large scale. In this connection it is also noteworthy that, equally as the Swedes make their tar from firwood, I have here in England made from pit-coal a sort of tar which is equal to the Swedish in every way and for some operations is even superior to it. I have made proof of it on wood and on ropes, and the proof has been found right, so that even the King has seen a specimen of it, which is a great thing in England, and the coal from which the tar has been taken out is better for use than before." We have seen above that Becher protected his invention by letters patent.

Later on Clayton (1737–38) made some statements on the nature of the products obtained by destructive distillation; besides coke and tar he found that combustible gases were formed at the same time.

About the middle of the 18th century the use of coal became more general, and more especially the manufacture of coke for smelting purposes, in lieu of wood-charcoal, began to be practised on a more extensive scale. It is most remarkable that, in the infancy of coke-making, a process was practised which has

* "Närrische Weisheit, No. 36," quoted by G. Schultz, 'Chemie des Steinkohlentheers,' 2nd ed. p. 5, and faithfully translated here.

only during the last few years again come to the fore, namely the recovery of tar. A French metallurgist, de Gensanne, describes and figures a kind of muffle-furnace for coking coal and recovering tar, which was working at Sulzbach, near Saarbrücken, before the year 1768 *. From the description of the tar or "oil" obtained at Sulzbach (it is said to resemble distilled petroleum and was used for burning in peasants' and miners' lamps), it must have been much nearer in quality to the blast-furnace and the "Jameson" tar (to be mentioned hereafter) than to gas-tar or to the tar now-a-days obtained from closed coke-ovens. Gurlt points out that the "Kohlenphilosoph" Stauf (a visit to whose lonely forest-cottage near Saarbrücken, in 1771, is vividly described by Goethe, then a student of Strasburg University) seems to have been the originator of that coking-process: he produced from it "oil," bitumen, lamp-black, and had also collected a cake of sal ammoniac from the "burning hill" near by.

One of the patents of that indefatigable inventor the Earl of Dundonald (No. 1291, of April 30, 1781) describes an invention for coking coal, intituled "A method of extracting or making tar, pitch, essential oils, volatile alkali, mineral acids, salts and cinders from pit-coal." The condensation of the volatile portion is effected by mixing steam with it and then applying cold water. This invention does not, however, seem to have been worked out on a very large scale; at any rate it must have soon fallen into disuse.

In any case it is certain that the manufacture of coal-tar was never carried out on any extensive scale until it appeared as a necessary by-product in the manufacture of illuminating-gas from coal, the idea of which seems to have occurred, towards the end of the last century, at the same time to the Frenchman Lebon and the Englishman William Murdoch. The former had already recommended the use of tar for preserving timber; but it was the latter who, along with his celebrated pupil Samuel Clegg, really laid the foundation of the enormous industry of gas-making. The first private gas-works was erected in 1798 at the engineering works of

* De Gensanne, 'Traité de la fonte des Mines,' Paris, 1770, vol. i. ch. 12; quoted by Gurlt, 'Die Bereitung der Steinkohlen-Briquettes,' 1880, p. 22. The place is called "Fischbach" here, but "Sulzbach" occurs in the communications made by Gurlt to Mr. Watson Smith, and quoted in the 'Journal of the Society of Chemical Industry,' 1884, p. 602.

Bolton and Watts; the first public gas-works in London in the year 1813, in Paris 1815, in Berlin 1826.

The tar formed in the manufacture of coal-gas necessarily forced itself upon the notice of the gas-manufacturer, since it could not be thrown away without causing a "nuisance." It was probably from the first burnt under the retorts; but the method of doing this without giving very much trouble was not understood then. Other quantities no doubt were used in lieu of wood-tar, as a cheap paint for wood or metals; but it must have been soon found out that in the crude state it is not well adapted for this purpose, as will be shown later on. It was also quickly perceived that in this respect tar is improved by boiling it down to some extent; and as early as 1815 Accum showed that, if this boiling down is carried out in closed vessels (stills), a volatile oil is obtained which may be employed as a cheap substitute for spirits of turpentine. But this does not seem to have been carried out to any great extent; and coal-tar remained, for more than a generation from the first introduction of gas-lighting, a nuisance and hardly anything else.

In Germany the first more extensive employment of gas-tar was for making roofing-felt, for which purpose it has to be deprived of its more volatile constituents. Instead of condensing these, they were at first almost everywhere, and later on in many cases, removed by evaporating the tar in open vessels, thus creating a considerable risk from fire. In Germany, Brönner, of Frankfort, was the first (in 1846) to condense the more volatile tar-oils, from which he prepared a detergent, long after known by his name, and consisting principally of benzene.

In England, where the manufacture of illuminating-gas originated, and where it has always been, and still is, carried on to a very much greater extent than on the continent, a more extensive industrial employment for coal-tar was first opened out by the invention of Bethell (1838) for preserving timber, especially railway-sleepers, by impregnation with the heavy oil distilled from gas-tar. From that time dates the introduction of tar-distilling on a large scale. The light oils may have been lost even here in some cases; but more usually they were condensed and employed as "coal-tar naphtha" for burning and for dissolving india-rubber.

The day of the light tar-oils came after A. W. Hofmann (1845) had shown the presence of benzene in them, but especially when

Mansfield (whose researches will be mentioned in detail hereafter), in his patent-specification (1847), for the first time accurately described the composition of those oils, along with a process for preparing benzene in a pure state and on a large scale, and with proposals for utilizing the tar-oils of lowest boiling-point for lighting-purposes. The industrial preparation of benzene was soon followed by that of nitrobenzene, at that time only employed as a substitute for the essential oil of bitter almonds, and known by the French fancy name "essence de Mirbane." But all these applications produced only a limited demand for the light oils which could be made from the rapidly increasing quantities of gas-tar; so that the latter, except in a few instances locally, did not attain any considerable commercial value. But a sudden impetus was given to tar-distilling in 1856 by the discovery of the aniline colours, the material which forms their starting-point, benzol, being exclusively derived from coal-tar.

In the centres of industry, where at the same time most gas is made, coal-tar was at once converted from a nuisance into a commercial article in great demand at good prices. Although only about one per cent. of the tar is obtained as benzol, this article at first yielded so much that the other products of tar-distilling could be sold at low rates and new markets could be opened out for them. It is true that, as usual, excessive competition led at one time to a great fall in the price of benzol; and as at the same time the sale of creosote-oil and pitch was very poor, tar-distilling seemed to be hardly a remunerative business. But this state of affairs passed away. Even at that time a more rational utilization of the by-products permitted working at a profit; and this, so long as tar is at a reasonable price, was fully secured when, through Graebe and Liebermann's discovery of artificial alizarin, anthracene attained a much higher value than any other product from coal-tar.

In the course of time the following state of affairs has established itself. In England, where by far the largest quantity of gas-tar is produced, where benzene was discovered by Faraday, its industrial preparation by Mansfield, the first aniline colour by Perkin, and where the conditions are the most favourable for the purchase of the necessary chemicals as well as for the sale of the colouring-matters, the manufacture of artificial dyes has only risen to moderate dimensions. The same has been the case in France. On the other hand, in Germany and Switzerland the manufacture of

coal-tar colours has been established on an enormous scale, so that the tar produced there can only supply a small portion of the benzol and anthracene required, most of it being imported from England and France, partly in the form of aniline. But the employment of the other coal-tar products, especially dead oil and pitch, in Germany has by no means increased *pari passu* with that of benzol and anthracene; the former, very cheap, articles frequently have to seek markets at such distances that the expense of carriage becomes excessive. Moreover, gas-making in Germany is only partially concentrated at a few large centres of industry; very many small gas-works are scattered all over the country, sometimes not even situated near a railway line, and hardly ever on the bank of a canal or navigable river; so that the collecting of tar for a larger tar-distillery does not pay. Hence in Germany and Switzerland, where the manufacture of coal-tar dyes has reached its greatest development, it frequently happens that the tar produced at the gas-works has to be burned under the retorts, a state of things which at this date (1886) has partially, but from other causes mentioned before, arisen in Great Britain as well.

Quantity of Coal-tar produced.

At the Hamburg meeting of German architects and engineers, in 1884, Gallois made the following statements concerning the production of gas-tar in some of the principal European countries, for the year 1883:—

	Number of gas-works.	Coal tar produced, tons.
Great Britain	452	450,000
Germany	481	85,000
France	601	75,000
Belgium	...	50,000
Holland	...	15,000
		675,000

G. Schultz ('Steinkohlentheer,' 2nd ed., 1886, p. 10) estimates the yearly distillation of coals for gas-making in Great Britain at 9 millions of tons, that of Germany at 2 millions of tons. [The former would correspond to about 450,000 tons of tar, which is undoubtedly too low, the latter to about 100,000 tons of tar.]

He also states that the yearly consumption of coal-gas per head of the population is :—

In Germany.....	350	cubic feet
France	560	„ „
England	2450	„ „
London	5000	„ „

Levinstein (J. Soc. Chem. Ind. 1886, p. 352) estimates the present yearly distillation of coal for gas-making in the United Kingdom at about 12 millions of tons, yielding about 144 million gallons of tar (=750,000 tons), and capable of yielding nearly 3 million gallons of 50-per-cent. benzol (=11,650 tons), with a yearly increase at the rate of from 5 to 7½ per cent. This estimate would appear to be rather too high. Another estimate, by Mr. Wilton, of the Beckton Tar-works, puts the quantity of tar actually distilled in the United Kingdom in 1885 at 120 million gallons, averaging 12 lb., or about 643,000 tons (private communication). Wanklyn, in the 'Gas-Engineer's Chemical Manual,' p. 1, estimates the quantity of coal distilled for gas-making in the United Kingdom at 10 millions of tons, one fifth of this being cannel coal; the capital invested in gas-works he states =£70,000,000, the yearly receipts for gas and by-products =£20,000,000.

From an annual analysis of the accounts of the principal English Gas Companies, published by Mr. John Field (obtained through the kindness of Mr. S. B. Boulton), it appears that the following quantities of coal were carbonized in 1884 and 1885 :—

	Coal carbonized, tons.		Tar made per ton, gallons.	
	1884.	1885.	1884.	1885.
3 Metropolitan Companies ...	2,200,659[1]	2,325,176[4]	10·7	10·7
14 Suburban Companies	327,452[2]	325,217[5]	10·1	10·2
8 Provincial Corporations.....	986,498	1,083,026[6]	12·7	12·6
10 „ Companies	906,655[3]	948,475[7]	12·1	12·0

[1] 44,847 tons cannel coal.
[2] 13,384 tons cannel coal.
[3] 183,345 tons cannel coal.
[4] 49,319 tons cannel coal.
[5] 10,397 tons cannel coal.
[6] 339,960 tons cannel coal.
[7] 189,499 tons cannel coal.

It should be noticed that the London gas companies consume but little cannel coal, not much over 2 per cent. of the total amount of coal distilled; whilst the Manchester Corporation gas-works in 1885 consumed 216,302 tons of cannel to 64,292 tons of common coal, and the Liverpool Gas Company 138,469 of the former to 138,188 of the latter. This accounts for the fact that country tar is much lighter than London tar, and that the yield of the former from a given quantity of coal is greater than that of the latter.

According to estimation, supplied to the author on the spot, the quantity of coal-tar distilled in 1886 in Holland was 20,000 or 22,000 tons, in Belgium about 30,000 tons per annum.

The following notes on the production and consumption of coal-tar in the *United States* are due to a private, but trustworthy, communication from Mr. A. von Schauer. The total production of coal-tar in the United States amounts to 500,000 barrels at 50 gallons each per annum [say 120,000 tons]. Of this quantity 250,000 barrels [say 60,000 tons] are distilled, 150,000 barrels [say 37,000 tons] are employed for manufacturing roofing-paper, roof-coating, and similar compositions, and 100,000 barrels [say 23,000 tons] are used up in the raw state. The most extensive tar-works are situated at New York, Philadelphia, Boston, Erie, Cleveland, Pittsburg, St. Louis, Chicago, and Baltimore. The five first-named also refine the products of distillation and produce benzol, carbolic acid, and naphthalene, but there is very little anthracene made. Benzol is mostly made as 30 or 50 per cent.; the production amounts to 5000 barrels [say 250,000 gallons or nearly 1000 tons], part of which is consumed by the only aniline-colour works in the States (Messrs. Schöllkopf and Co.), while the remainder is exported in iron barrels to England. The manufacture of and demand for pure naphthalene are increasing. Creosote oil for pickling timber is used only in some of the Southern States, where timber is not plentiful, *e. g.* at Norfolk in Virginia and at New Orleans. The manufacture of patent-fuel (briquettes) does not seem to be carried on, owing to the cheapness of coal and the great extent to which the gas spontaneously issuing from the ground in various localities is utilized, both as fuel and for lighting-purposes. The latter circumstance, combined with the spreading of the electric light and of lighting by water-gas, tends to diminish the manufacture of ordinary coal-gas, and therewith the production of gas-tar.

CHAPTER II.

PROCESSES FOR OBTAINING COAL-TAR.

A. *The Production of Coal-tar at the Gas-works.*

Formerly nearly the whole of the coal-tar was obtained, and even most of it is so now, as a by-product in the manufacture of ordinary coal-gas for illuminating-purposes, and formerly, therefore, the denominations "coal-tar" and "gas-tar" were practically identical, and were both in constant use. Since the manufacture of coal-tar from other sources has become practicable, although not to the extent expected a few years ago, we must distinguish as "gas-tar" that particular kind of coal-tar which is obtained in the process of gas-making as an involuntary by-product.

It is not within the scope of this treatise to give a description of the ordinary contrivances for condensing the tar, which belong entirely to the domain of gas-making. It is sufficient to mention that the constituents of the tar escape from the gas-retorts in the form of vapour, with a little solid free carbon in an extremely finely divided state; they are precipitated in the hydraulic main, in the condensers, scrubbers, &c., in a liquid state, at the same time as the ammoniacal liquor is formed. In one particular instance *, of 100 parts of tar altogether obtained, there was found 61·6 in the hydraulic main, 11·8 in the condenser, 26·6 in the scrubbers. The tar formed in the hydraulic main is, of course, poorer in the more volatile products than that formed in the condensers and scrubbers, and is consequently much thicker than the latter; but it is usual to mix all these descriptions of tar in the cistern where they collect, along with the ammoniacal liquor.

* Schultz, 'Steinkohlentheer,' 2nd ed. i. p. 43.

The quantity and, to a much greater extent, the quality of the tar are influenced by the *temperature* at which the decomposition of the coal is carried on. Low temperatures, with 9000 cubic feet of gas per ton of coal, will yield, with some coals, 16 gallons of tar; whilst high temperatures will yield but 9 gallons, with about 11,000 cubic feet of gas, from the same coal*. If the temperature be a comparatively low one, mostly such hydrocarbons are formed as belong to the paraffin (methane) series, having the general formula C_nH_{2n+2}, along with olefines, C_nH_{2n}. The lower members of these series are liquid, and, furnished in the pure state, are lighting- and lubricating-oils; the higher ones are solid and form commercial paraffin. They are always accompanied by oxygenized derivatives of the benzene series (phenols); but of these the more complicated ones predominate, in some of which methyl occurs in the benzene nucleus, in others replacing the hydrogen of hydroxyl:—*e.g.* cresol, $C_6H_4(CH_3)(OH)$; guaiacol, $C_6H_4(OH)(OCH_3)$; creosol, $C_6H_3(CH_3)(OH)(OCH_3)$, &c. Liquid products prevail; and among the watery ones acetic acid (which is again a compound of the fatty series) is paramount. Of course also permanent gases are always given off, though in comparatively small quantity.

If, on the other hand, the coal has been decomposed at a very high temperature, the molecules are grouped quite differently. Whilst the olefines and members of the acetylene series still occur more or less, the hydrocarbons of the paraffin series disappear almost entirely; and from them are formed on the one hand compounds much richer in carbon, on the other hand more hydrogenized bodies. The latter always occur in the gaseous state; hence the gas so produced contains methane or marsh-gas, CH_4, and free hydrogen as principal constituents, and is very much increased in quantity. The carbon thus set free is partly deposited in the retorts themselves, and then occurs in a very compact graphitoidal form; another portion of the free carbon occurs in a state of extremely fine division in the tar, and forms a constituent of the pitch or coke remaining behind from tar-distilling; another portion contributes to the formation of compounds richer in carbon, belonging to the "aromatic" series, all of which are derived from benzene, C_6H_6. At the same time the action of heat effects further molecular "condensations," usually with separation of hydrogen, by which process compounds of a higher molecular

* Davis, Journ. Soc. Chem. Ind. 1886, p. 5.

weight are formed, as naphthalene, anthracene, phenanthrene, chrysene, &c. The never absent oxygen must also in this case cause the formation of phenols; but here phenol proper, or carbolic acid, $C_6H_5(OH)$, predominates, whilst cresol and the other homologues are diminished in quantity, and the bioxy-benzenes, as well as their methylated derivatives, disappear altogether.

The above will be better illustrated by the statement* that Zwickau glance coal yielded the following quite different products, according to whether it was put into a cold retort and gradually brought to a red heat (*a*), or distilled quickly from a very hot retort (*b*) :—

	a.	*b.*
Coke	60	50
Water	10·7	7·7
Tar	12	10
Gas and loss	17·1	32·1

The tar from *a* consisted of photogen, paraffin oil, lubricating-oil, paraffin, and creosote; that from *b*, of benzene, toluene, naphthalene, anthracene (together with heavy oils corresponding to the paraffin and lubricating-oil), and much creosote.

Behrens† found that the tar obtained in the distillation of coal in the ordinary fire-clay gas-retorts was much richer in benzene, toluene, naphthalene, &c. than the tar made in Pauwels' coke-ovens from the same kind of coal. The latter is of less specific gravity, and contains more liquid (paraffinoid) hydrocarbons, also far more substances soluble in alkalis, but hardly any carbolic acid. We shall further on treat in detail of the differences between tars obtained in different processes of coal-distilling, carried on for other purposes than gas-making.

The same cause explains the difference between the tar of wood-gas-works, that of wood-vinegar-works, and that of charcoal-heaps (*Meilers*). The former, produced at a very high temperature, is black, thin, smells almost like coal-tar, and contains much real phenol, along with benzene, toluene, naphthalene, &c. The tar obtained at a lower temperature, especially that from the charcoal-heaps, contains mostly cresol and guaiacol in the place of phenol, and paraffin instead of naphthalene; it has a lighter brown colour and a much milder smell.

* From Stohmann-Kerl's 'Chemie,' 3rd ed. vi. p. 1162.

† Dingler's 'Polyt. Journal,' vol. ccviii. p. 362.

A further difference between distillation at high and at low temperatures is stated to consist in the fact that most of the nitrogen appears in the former case in aniline and fatty amines (ethylamine, propylamine, amylamine), in the latter case in bases of the pyridine series, along with picoline, lutidine, viridine, &c. But this requires to be verified by more detailed investigations.

Of course it is not possible to get the above products in any desired quality from any one of the raw materials here concerned, merely by altering the temperature of the dry distillation. It has, for instance, been doubted whether real benzene can be obtained at all by direct distillation from more recent deposits, as peat, browncoals, some sorts of bituminous shales, &c.; and these materials in no case serve for a profitable extraction of benzene and the other aromatic hydrocarbons. Wigan cannel coal, if used alone, instead of, as is usual, being mixed with less bituminous coals, yields tars containing so much paraffin that no tar-distiller will take them (*Watson Smith*). On the other hand, photogen, paraffin oil, &c. cannot be profitably made from coal by distillation at a lower temperature*; for cases like that of the Zwickau coal, mentioned above, do not furnish a rule for industrial practice, which has proved that even among browncoals only certain light, earthy descriptions ("Schweelkohle") are adapted for the manufacture of lighting-oils. But we shall see that it is at least in our power, by *subsequent overheating*, to split up the fatty products (paraffins) from browncoal and petroleum, to a great extent, into gases and aromatic compounds; and to this, no doubt, the illuminating-power of oil-gas and the gas made from petroleum-residues is mainly due.

Our present task lies only with the treatment of real coal. We must remember that at a lower temperature less permanent gases and more methylated derivatives (toluene, xylene, higher phenols), at a higher temperature more gases, along with benzene, naphthalene, anthracene, and far more free carbon, are formed. At very high temperatures the tendency to complete dissociation becomes far more pronounced; the products approach more and more to free carbon on the one hand, and free hydrogen on the other; but this end itself is never actually reached at the temperatures attainable

* Professor Dittmar, of Glasgow, informs me that, twenty-four years ago, at Manchester, oils of the formula C_nH_{2n+2} were made by the distillation of coal at a low temperature. But no doubt this was cannel coal, which in that respect occupies a place between real coal and younger fossils.

to us. Most gas-engineers try above every thing to get as much gas as possible out of the coal, and therefore distil at the highest possible temperature. Up to a certain point this is quite rational, and is even unavoidable from the nature of the material now universally employed for gas-retorts, viz. fireclay. This point seems to be reached when the fatty compounds are split up as far as possible, before any considerable separation of free carbon has taken place. Beyond this point more gas will be got; but its lighting-power will be less; the tar will at first contain a little more of the valuable anthracene, but at the same time even more of naphthalene, which has much less value, and of phenanthrene, pyrene, chrysene, diphenyl, &c., which are quite valueless; so that its value on the whole will be less. There is also a reduced quantity of tar, if the temperature in the retorts is raised higher. The separation of free carbon in the retorts and the tar is also largely increased. In England the usual temperature of working seems now to be about 1100° C. (=2000° F.). But, properly speaking, it should be experimentally ascertained (and that for every class of gas-coal specially) at what temperature the maximum of lighting-power is obtained, even if concentrated in a smaller volume of gas, and also at what temperature we can get a maximum yield of benzene, toluene, phenol, and anthracene in the tar. Probably the two maxima will not coincide; and it will then be a matter of business calculation whether the one or the other is to be worked for. It is evident that the market prices of the tar-products will influence this consideration largely, and that any diminution in the price of gas will turn the scale in favour of richer tar.

It is quite certain that the composition of coal-tar was very different from what it is now at the time when coal used to be distilled in cast-iron retorts, necessarily at a considerably lower temperature than the above-mentioned 1100° C., which applies to fireclay retorts. The higher temperature existing in the latter is certainly to some extent counterbalanced by the action of the exhauster, which causes the gases to remain a shorter time in contact with the heated sides of the retort. The exhauster also makes the tar thicker, by carrying away a good deal of coal-dust from the retort.

Some statements on the influence of the *shape* of the gas-retorts and exit-pipes on the quality of the tar have been made by Hayes*. If the shape of the retorts be such that the volatile products are

* Silliman's Amer. Journal, March 1859.

carried away from the hottest place through a narrow pipe, much less heavy and much more light oil is said to be obtained; the coke is then much more compact and harder. Even a slight modification of the width of the pipe is said to influence the nature of the products.

That the difference of quality of the coal influences the quantity of valuable constituents of the tar, is a matter of course. Newcastle coals furnish tar rich in naphthalene and anthracene, Wigan coals tar containing much benzol and phenol. Among German tars that from Silesian coal is greatly superior in quality to that from Westphalian coal. It is especially injurious to the quality of the tar if the lighting-power of the gas is augmented by addition of *boghead* or any similar *bituminous shales* to the coal. In such a case, even at the highest practical temperature, hydrocarbons of the paraffin series appear more extensively in the tar. The benzol will contain hydrocarbons similar to petroleum-spirit, and the anthracene paraffin, neither of which impurities can be removed by the methods usually practised, viz. fractional distillation or crystallization. Hence many tar-distillers stipulate in their contracts that the gas-works must not mix more than 5 per cent. of shale (boghead &c.) with their gas-coal.

Besides paraffins, boghead tar contains principally toluene and naphthalene, and but little benzene and anthracene. The real boghead, or Torbane-hill mineral, is now practically exhausted; but the name is still used in commerce for shales of much inferior value. The shale-spirit got from these contains, along with the paraffins, very sensible quantities of benzene and toluene *.

Through the kind mediation of Professor Dittmar I have received the following information from Dr. Ronalds on the tar from *cannel coals* and *boghead*. Scotch cannels were exclusively used in Edinburgh and Leith, and probably in most parts of Scotland, for making gas prior to the coal famine in 1851–53, when many companies took to using common splint coal, and some attempts were even made to use shale mixed with coal. Shales give little or no tar; and the naphtha (if *any*) is similar to that from boghead (the hydride series). The quality of the tar now made from the various kinds of cannel coal (such as those from Lismahago, Marquis of Lothian, Arnichar, Benhar, Walleford, and numerous other localities) is very different from that obtained formerly.

* Watson Smith, private communication.

Twenty years ago, when *low* heats were used at the gas-works, as much as 8 per cent. of naphtha (*i. e.* benzene and its homologues) was obtained by distillation with steam. This diminished slowly as the heat employed at the gas-works increased, until it had fallen a few years ago to about 3 per cent. The naphtha from Scotch tar was always rich in toluene, and contained less benzene than that from ordinary bituminous coal. It contains little naphthalene and very little anthracene—so little of the latter that its extraction is not worth while. It also contains considerable quantities of paraffins, but mostly of low melting-points. Naphthalene and paraffin seem to go together; wherever there is much of the one, the other is almost always present too. When shale or boghead or similar semicoals are mixed with cannel or bituminous coal, the light naphtha is a mixture of the benzene and of the methane series; as these are very difficult to separate, the benzol is comparatively valueless as a commercial product. The heat used in the making of the gas and tar appears to have quite as much, if not more, to do with the quality of the products as the quality of the coal has.

A special investigation by Dr. Bunte * has shown the influence of the quality of coal on the quality and quantity of gas, tar, and ammonia produced in distillation. We extract from it the following statements (partly translated into English measures). The five descriptions of coals distilled had the following composition :—

Description of Coal.	Total contents of the Coal.					Composition of the organic substance.		
	C.	H.	O (+N & S).	Water.	Ash.	C.	H.	O (+N & S).
Westphalian (Consolidation)	78·94	5·22	7·59	1·64	6·62	86·04	5·69	8·27
Saar (Heinitz I.)	77·18	4·97	9·27	2·00	6·48	84·44	5·43	10·13
Bohemian (Thurn and Taxis)	71·97	5·36	10·18	5·61	6·88	82·25	6·12	11·64
Saxon (Zwickau) .	68·75	4·91	11·05	7·79	7·50	81·16	5·80	13·04
Bohemian Cannel coal (Pilsen) ...	67·41	5·98	8·87	3·33	14·43	81·95	7·27	10·78

These coals, when distilled in an ordinary gas-retort, fitted up with special condensing-apparatus for experimental purposes, but

* 'Journal für Gasbeleuchtung,' 1886.

otherwise working entirely under normal manufacturing conditions, yielded, as an average of a number of trials, for each 100 kilog. of coal, the following products:—

Description.	Coke, kil.	Gas.				Temp. of retorts, ° C.	Tar, kil.	Amm. Liq., kil.	Loss, kil.
		kil.	cub. metr.	cubic feet per ton.	Ill.-pow. candl.				
Westphalia ...	71·4	16·95	30·33	11,899	11·15	1360–1385	4·09	4·44	3·12
Saar	68·3	17·71	30·18	11,835	10·27	1205–1290	5·33	6·90	1·76
Bohemia.....	63·3	18·52	28·47	10,221	10·20	1240–1350	5·79	9·06	3·33
Zwickau.....	62·7	15·81	25·46	9,140	10·59	1180–1240	5·22	11·89	4·38
Boh. cannel ...	56·3	25·72	30·38	11,916	18·17	1180–1350	8·81	6·45	2·72

This seems to show that the quantity of tar increases with the percentage of oxygen in the coal, apart from the necessarily different case of cannel coal. The increase of the yield of ammoniacal liquor is in the same direction; but this proves nothing, as neither the strength of the liquor nor the original percentage of nitrogen in the coal is stated.

Bunte's results have been completely confirmed by the report of the 1012 trials made, on a working scale, by the Paris Gas Company from 1874 to 1884, with 59 different classes of coal *. The conclusions arrived at are:—"The higher the percentage of oxygen, the more tar and ammonia is formed and the more hygroscopic water is contained in the raw coal; on the other hand, the yield of coke and gas is less with a rise in the percentage of oxygen."

The theory of the formation of tar in the distillation of coal is too uncertain to be treated at length in this place. We know from the researches of very many chemists, beginning with Priestley, but the most prominent of whom is Berthelot, that most organic bodies, also those of the fatty series, furnish aromatic compounds (benzene and its homologues, naphthalene, anthracene, &c.) when exposed to a very great heat, especially when brought into contact with a red-hot or white-hot tube. But, on the other hand, those same aromatic products are decomposed by higher degrees of heat, and ultimately furnish free hydrogen, along with free carbon, or else compounds so rich in carbon that they have

* 'Journal de l'éclairage au Gaz,' juillet 1886.

been hitherto indistinguishable from it. But the different stages of these processes are extremely complicated, and the attempts at explaining the formation even of the better-known constituents of coal-tar by means of some plain reactions of a few simple compounds, such as acetylene, allylene, &c., do not seem to be very convincing. The problem of the theory of destructive distillation has been approached from a different side by E. Mills (Journ. Soc. Ch. Ind. 1885, p. 325). His argument turns upon the point that the process by which cellulose, $nC_6H_{10}O_5$, is turned into coal is essentially one of dehydration; so that, for instance, by heating wood to 430° without pressure, the residue has the composition nC_6H_2O; and he assumes that in any case the organic matter in coal, shale, &c. corresponds to an initial symbol nC_6 or $2nC_3$; also that a definite relation exists between the C of the fixed carbon on the one hand and the C of the gas + tar on the other hand, in which C_3 is always the fundamental unit. We must refer for details to the original, merely pointing out two oversights in that reasoning (which, of course, were quite well known to the author), namely, that woody fibre is not at all $=nC_6H_{10}O_5$, the formation of oxycellulose, lignin, &c. having intervened, and that the formation of coal from woody fibre is anything but a mere dehydrating process—CO_2, CO, CH_4, and other carbon compounds being liberated at the same time as water.

The total yield of tar from the coal may be set down on the average as 5 per cent. on the weight. Wanklyn ('Gas-Engineer's Chemical Manual,' p. 5) states that one ton of coking-coal (Newcastle coal) yields

	lbs.	per cent.
10,000 cubic feet of gas	380	17·0
10 gallons of tar	115	5·1
Virgin gas-liquor*	177	7·9
Coke	1568	70·0
	2240	100·0

Exact figures concerning the yield of tar in London and provincial gas-works have been already given, p. 14. According to Wurtz †, St.-Etienne coal only yields 4 per cent. of poor tar, but Anzin and

* That is, the liquor condensing from the gas alone without any water running down within the scrubbers.

† Dictionn. de Chimie, i. p. 1631.

Mons coal 6·73 per cent., and "Prussian" coal up to 7 per cent., of rich tar. Of the German coals those from Upper Silesia yield the best, those from Westphalia the poorest tar. The yield of tar is given in the following Table*, which shows that from various descriptions of coal, along with that of other products, on the average there is obtained

	Tar.	Ammoniacal liquor.
from coal generally.....	4 to 6	6 to 10 per cent.
„ English coals	4·5	6 „ „
„ Silesian „	5 to 6	9 „ „

1 ton (2240 lb.).	Gas.		Coke.	Tar.	Gas-liquor.	Loss.
	cubic feet.	lb.	lb.	lb.	lb.	lb.
Boghead cannel	13334	...	715	733·3		
Newcastle	9833	...	1426	98·3	60	
Wigan cannel	10850	...	1332	218·3	161·6	
Lochgelly	8331	...	1245	225	340	
⅛ Lochgelly + ⅞ boghead	9055	...	1200	400	170	
⅛ „ + ⅛ „	9050	...	1205	335	290	
⅛ „ + ⅛ „	9750	...	1240	227	270	
Pelton Main (Durham)	9500	...	1540	112·5	112·5	
¾ „ + ¼ boghead	12800	...	1366	206·6	116·6	
Lismahago cannel, I. ...	11681	461	1091	594	4·5	87·5
„ „ II....	9878	483·5	1064	603	4·5	85
Ramsay's N'castle cannel	9016	410	1435	295	6·7	93·3
Derbyshire deep-seam ...	9400	300	1335	219	179	207
Wemyss cannel, I.	10976	551	1124·5	224	...	340
„ „ II.....	10192	528	1188	197	...	327
Wigan cannel	9408	338	1326	250	...	326

Proposals for Increasing the Quantity or Improving the Quality of Tar in the Manufacture of Coal-gas.

We have already seen that both the quantity and the quality of tar differ with the quality of the coal and the temperature of distilling it, no doubt also with the pressure existing in the retort and the velocity with which the gases are evolved and are made to escape from the retorts. All these conditions, however, must in the first instance be made subservient to the aims of manufacturing illuminating-gas; that is, obtaining the best yield and the best quality of gas, the tar being left to take its chance. This was the

* Stohmann-Kerl's 'Chemie,' 3rd ed. iv. p. 624.

case even at the time when the by-products nearly paid for the whole process; and at the present time, when tar and ammonia have become depreciated to such an extent, it cannot possibly be otherwise. Still it may be possible to introduce such improvements as will serve the purpose of improving the yield or the quality of the tar, and the following proposals have been made with this object:—

H. Aitken (B. P. 4644, 1883) considers that the large amount of water contained in certain kinds of coal, shale, and lignite (real coal does not contain much water) causes the coke to be too porous and light and carries off much of it in the unburnt state. He therefore dries the coal in a tower by drawing or blowing heated air or hot products of combustion through it. The coal thus treated is stated to yield much closer and heavier coke, a higher yield of gas, and tar containing more benzene. [Although this process might do for very moist materials, it would certainly not pay in most ordinary cases.]

N. A. Hélouis, of Paris, evidently inspirited by the reading of Berthelot's and other great savants' researches, but without much regard to the conditions and requirements of practical work, obtained provisional protection (B. P. 5142, 1883) for a process based on the "rational and permanent production of acetylene." This is to be attained: 1, by a fixed temperature never exceeding a dull red-heat in the retorts [!]; 2, by the permanent action of a current of previously superheated gas and steam led into the retorts during the whole time of the distillation; 3, by maintaining a mean pressure of $\frac{1}{3}$ atmosphere in the retorts. Thus acetylene, the [altogether hypothetical!] generator of benzene, is to be permanently produced, whilst the benzene itself is protected against being condensed into more complex carburets, constituting heavy oils of less commercial value.

Heusser (G. P. 24,728), also from purely theoretical considerations on the "condensing" action of acids, zinc chloride, &c., believes it possible to obtain at will hydrocarbons of a lower boiling-point by passing chlorine gas and hydrochloric acid vapour into the gas-retorts; and hydrocarbons of a higher boiling-point by mixing the coal with zinc chloride, with or without the admixture of tar or tar-oils, and also passing hydrochloric-acid vapour into the retorts during the dry distillation. It does not seem necessary to criticise this process.

Byrom, Wigan, and Bennett (B. P. 3736, 1884) propose removing the various products of distillation from the retorts before they are mixed, thus avoiding the expense of redistillation. This is to be done by providing the retort with a number of openings along its highest part, each exit-pipe being supplied with a bend which may be inclined downwards, the pipe being of sufficient length to secure the condensation of the liquid, the gases to be drawn off by an exhauster. This process, if at all feasible, would evidently apply more to the distillation of shale &c. for paraffin-oil than to that of coal for gas-making.

Kunath (Chemiker-Zeitung, 1885, p. 1893) attributes the thickening of tar not merely to the presence of particles of coal carried over mechanically with the gas, but principally to a local superheating of the gas. Thinner tar is to be obtained by charging the retorts with as much coal as possible, and thus reducing the gas-space and the contact surfaces.

We shall later on meet with several other attempts at improving the quality of the tar or increasing the quantity of its more valuable constituents by a special treatment while in the gas-retorts themselves or subsequently.

Proposals for obtaining Aromatic Hydrocarbons from Coal or Coal-gas, irrespective of the Value of the Gas for Illuminating-purposes.

Some of the following proposals start with treating the coal from the first in an appropriate manner for obtaining more benzene &c.; but others start from coal-gas as ordinarily obtained, subjecting this to a special treatment for depriving it of the hydrocarbons suspended like a fine mist or even contained in it as real vapour.

There are some older proposals for distilling coal specially for the purpose of tar-making (Barlow in 1862 and others). Thenius*, many years ago, proposed the employment of superheated steam for this object. We shall, however, principally treat of the more modern inventions in this direction.

Recovery of the Tar suspended in the Gas.

Ordinary coal-gas always contains a good many tarry particles

* Wagner's Jahresb. 1865, p. 738.

in mechanical suspension. These particles are to some extent precipitated in the gas-pipes, and are found both at the gas-works and in the "siphons" of the street pipes as oils or as masses of crystallized naphthalene. These oils have been examined in detail by Gasch*. He found that they gave off

3–6	per cent.	up to	100°,		
5–8	,,	from	100°	to	130°,
5–15	,,	,,	130°	,,	150°,
19–36	,,	,,	150°	,,	180°,

on the whole, 47–76 per cent. up to the point where naphthalene appeared. They contain numerous sulphur compounds—below 100° carbon bisulphide, above 100° probably mercaptanes. An exact examination of these oils (which do not appear to be systematically collected anywhere) is yet wanting.

The quantity of tar can be considerably increased by supplementing the condensing-action of the air-condensers and scrubbers by more efficient apparatus. This is the object of the process of Pelouze and Audouin †, which is being worked very successfully at Paris. That they are not the real inventors of the process has been decisively proved by Colladon‡. The invention proceeds from the principle that mere cooling cannot possibly condense all the tar, because the latter remains mechanically suspended in the gas in the shape of extremely minute liquid drops, *i. e.* in the form of a mist. A portion of this is retained in the coke-scrubbers, but very far from all of it. The result is different when the gas is made to issue through narrow apertures and impinge against a broad solid surface, over which it must spread. The fine liquid particles are thus brought into very much increased contact with each other and with solid bodies, gather into larger drops, and are thus retained. Fig. 1 shows how this principle is carried out. The gas passes into a vessel A through the inlet-pipe B, and leaves it at C. Inside A is a cylinder D, the proper purifying-apparatus, which floats in the hydraulic tar-lute E, so that the gas can only get from B to C through the perforated sides of D. The latter are made of three concentric sheets of brass, $\frac{1}{16}$ inch apart, and perforated with many holes. The holes *a a* (fig. 2) are $\frac{1}{16}$ inch wide, arranged in

* 'Journal für Gasbeleuchtung,' 1873, p. 65; Wagner's Jahresb. 1873, p. 914.
† Compt. Rend. lxxvi. pp. 264, 928. ‡ Ibid. lxxvii. p. 819.

Fig. 1.

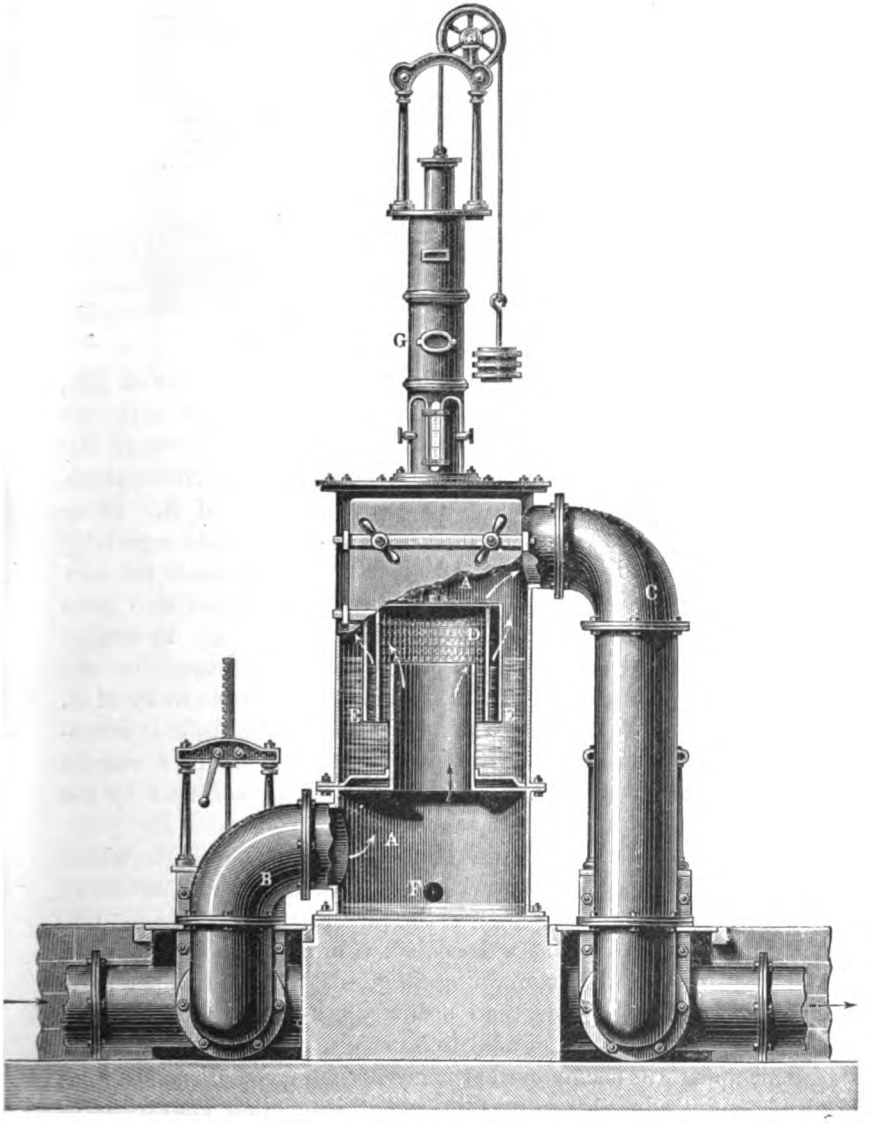
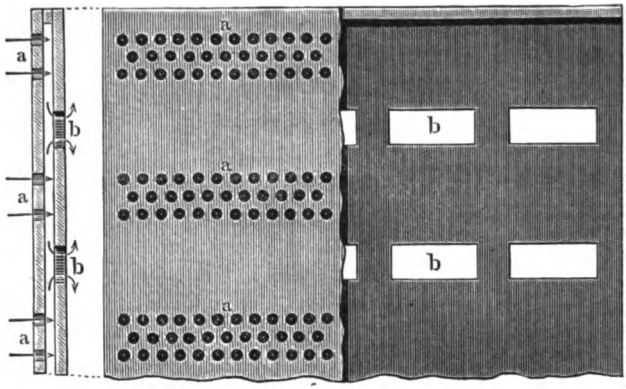


Fig. 2.



three rows placed transverse to each other, so that the jets of gas, issuing through the holes of the innermost plate, meet with the solid portion of the middle plate, and when issuing through the holes of the latter again meet solid portions of the outermost plate, from which at last they can get into the upper space of B. Since experience has shown that the holes of the middle plate especially are readily clogged up with tar, the apertures of this plate are now made (as shown in fig. 2) larger and square. It has also been attempted to replace the holes by vertical slits, which do not so easily get stopped up. The tar condensed by the impact on the plates runs into the tar-cistern E, flows over and runs away at F. Since of course some pressure is lost in this apparatus, it is necessary to let the gas, previously well cooled, issue under a certain surplus pressure, say $1\frac{3}{4}$–$1\frac{7}{8}$ inch, which is kept constant by the automatic regulator G.

In 1876 there were eight such condensers at work in Paris, which produced:—At the Ternes works, from each 1000 cubic metres of well-cooled gas, 9 kilog. of tar; at the La Villette works, from 1000 cubic metres of gas not so well cooled, as much as 72 kilog. of tar, and 16 litres of liquor containing 80 grams of ammonia per litre. The tar is much lighter than ordinary gas-tar; it yields 20 per cent. of light oils, instead of 3 to 5 per cent.

This apparatus is employed at many French gas-works, and it has also been introduced to a certain extent into other countries, for instance into Germany; but it has not made its way there, probably

because it is very difficult to keep the holes from being clogged up, and because it is doubtful (at present more than ever) whether the extra yield of tar is not counterbalanced by the loss in the illuminating-power of the gas.

Recovery of Benzene &c. contained as Vapour in Coal-gas.

It has long been known that a good deal of benzol is contained in coal-gas, and adds much to its illuminating-power. According to the extensive experiments made by the Paris Gas Company (*suprà*, p. 23), the percentage is pretty constant in the case of the various descriptions of coal, and amounts upon 1 cubic metre of gas to 30 grams of benzene and 9 grams of toluene &c.; by volume to 1·05 per cent., along with 2·5–4·8 per cent. by volume of heavy hydrocarbons belonging to the fatty series. The benzene &c. is precipitated when cooling down the gas to −70° C., whilst the other heavy hydrocarbons remain in the gaseous state. From this we may make the following calculation:—One ton of coals yields about 11,000 cubic feet or, say, 300 cubic metres of gas, containing 11·7 kilog. of benzol &c. At the same time about one cwt. of tar is formed, from which about 0·5 kilog. of benzol is obtained. *Hence coal-gas contains 23 times as much benzene &c. as the tar formed from the coal at the same time*; and this is a very legitimate stimulus for attempts to recover benzol from coal-gas.

S. Mellor (B. P. 5604, 1882) proposes to obtain benzol, toluol, or their homologues by *subjecting coal-gas to a pressure of four or more atmospheres*, whereby those hydrocarbons are to be deposited in a liquid form. This proposal is manifestly impracticable, if it is intended to be applied to ordinary coal-gas. But it seems a different matter when we consider the "rich" gas obtained from petroleum, fatty oils, &c., and subjected to several atmospheric pressures, in order to light railway-carriages and the like. In this case liquids are spontaneously condensed, and it needs only to be called to mind that Faraday, in 1825, discovered benzene in a liquid condensing from compressed oil-gas. Greville Williams (B. P. 4663, 1884) treats such liquids in the following manner:—They are distilled, and all coming over below 65°·5 is rejected. The second portion is collected between 65°·5 and 87°·5, the third portion above 87°·5. To separate benzene (toluene &c.) from these distillates, they are subjected to the action of dilute nitric acid (100

gall. require 50 gall. commercial nitric acid and 50 gall. water), or of a mixture of sodium nitrate and sulphuric acid (190 lb. commercial nitrate of soda, 218 lb. commercial oil of vitriol, and 24½ gall. water to 100 gall. oil). The mixture is then distilled in a salt-glazed stoneware still by means of a steam- or water-bath; benzene and its homologues readily come over, the homologues of olefiant gas being converted into compounds, which remain behind in the still. The scientific principles underlying this proposal have been discussed by Gr. Williams in the 'Chemical News,' vol. xlix. p. 197. He found that the liquid obtained in manufacturing the "Pintsch gas" contained from 65·6 down to 24·6 per cent. of benzene and toluene, according to its specific gravity, which varied from 0·850 to 0·760. It should be noted that a process involving the distillation of liquids containing a large quantity of free nitric acid, and then necessitating the use of stoneware stills, must present a good deal of inconvenience.

Armstrong* has also subjected to examination the liquids condensing from Pintsch gas and some other descriptions of compressed gas made from oil or petroleum. These liquids, commonly called "hydrocarbon," are practically free from paraffins; they essentially consist of benzene and toluene (rarely less than 50 per cent.), of the dimethyl- and trimethyl-benzenes occurring in coal-tar, of naphthalene, of the hydrocarbons of the olefine and "pseudo-olefine" series (viz. ethylene, propylene, amylene, hexylene, and heptylene), and the "pseudo-acetylene" series (especially crotonylene, dimethylene-ethane, and isoallyl-ethylene). This "hydrocarbon," amounting to rather less than one gallon per 1000 feet of compressed gas, is not used by tar-distillers, as it is too difficult to separate the benzene and toluene from the other hydrocarbons; it is exported to Belgium, where it is said to be used for varnish-making. Entirely different from this liquid is the "tar" depositing from the oil-gas prior to its collection in the gas-holder, and amounting to about 5 gallons per 1000 feet of gas; it contains neither acids nor basic constituents, and little, or even hardly any, benzenoid hydrocarbons, but mostly undecomposed petroleum hydrocarbons—that is, the material started from.

Apart from compression, *cooling* to a very low temperature has also been proposed in order to condense hydrocarbons from coal-

* Journ. Soc. Chem. Ind. 1884, p. 462; Armstrong and Miller, Journ. Chem. Soc. vol. xlix. p. 74.

gas; but the objections to be made to this operation, if intended to apply to ordinary coal-gas, are quite obvious.

A second series of proposals refers to depriving either ordinary or specially prepared coal-gas of the particles of aromatic hydrocarbons suspended and contained as vapour in it, by *passing the gas through liquid absorbents* for those substances. Many years ago A. Vogel * passed the gas through colza-oil, which increased 20·5 per cent. in weight and very much in illuminating-power, whilst that of the gas did not suffer. The last statement is more than doubtful; it is now generally assumed that the illuminating-power of coal-gas is to a very great extent due to the presence of benzene vapours, the results of Berthelot† in this direction having been confirmed by many subsequent investigations of Frankland and other chemists. But if this be the case, the extraction of benzol may reduce the value of coal-gas to a greater extent than is represented by the value of the benzol recovered, minus the expenses entailed by the process. It has been proposed to replace the aromatic hydrocarbons taken out of the gas by "carburetting" with the vapours of petroleum-spirit and the like; but a widely extended application of this process is hardly practicable, nor is it likely that the same effect could be obtained with such impoverished coal-gas as has really been obtained with "water-gas" on the principle of the "incandescent" light, namely by introducing some solid body, as platinum, magnesia, zircon, &c., into the flame in order to give out light after having been raised to a white heat, for the reason that such poor gas does not give off sufficient heat to effect that purpose. This robbing the gas of one of its most valuable constituents is the great fault of all the processes devised for extracting benzol from ordinary coal-gas. That the light-giving constituents of coal-gas are almost entirely removed by passing it through heavy mineral oils was noticed in 1868 by Cusiter; but his observations were only made known to a very limited circle in 1874 ‡.

Whilst Vogel evidently did not aim at extracting benzol as such, this was the aim of a process devised by Caro, A. Clemm, K. Clemm, and Engelhorn (B. P. dated Feb. 17, 1869), during a period in which the price of benzol rose enormously. They brought the

* Dingler's Journal, vol. cliii. p. 464.
† Comptes Rendus, vol. lxxxiv. p. 571.
‡ Davis, Journ. Soc. Chem. Ind. 1884, p. 432.

gas into contact with oils of high boiling-points, such as petroleum, paraffin-oil, or fatty oils, and separated the benzene and toluene absorbed by subsequent fractional distillation, so that the residual oil could be used over again as an absorbent. This process did not hold its ground for any length of time, the decline of the price of benzol and the reduction in the value of the gas making it unremunerative.

In 1875 J. Barrow patented the application of artificial refrigeration to the collection of the vapours of solvent naphtha evolved in the working of india-rubber, afterwards absorbing them in oil—an idea which has since been utilized for a similar treatment of the benzene vapours contained in coal-gas.

In 1882 Caro's idea was once more taken up, first by J. Hardman (B. P. 4312, 1882), who began the process in the gas-retort itself, distilling at a very high temperature in order to produce more benzene and its homologues. These hydrocarbons are separated from the gas by means of condensing-apparatus, which are charged with anthracene oil or other heavy hydrocarbons. The gas, after this treatment, is rendered useless for illuminating, and is only fit for heating purposes.—We here meet with the idea that the manufacture of gas is to be treated as a secondary process, that of benzol being the primary object in view, to be promoted by a special treatment of coal.

A very similar course was taken by G. E. Davis (B. P. 5717, 1882; and 4468, 1883). He proposes ascertaining by experiment, for each particular kind of coal, the minimum temperature at which it will yield the maximum quantity of benzol without forming paraffins. This would be a lower temperature than in ordinary gas-making, and only 7000 to 8000 cubic feet of gas would be obtained from each ton of coal. Before charging into the retorts, the coal is to be moistened with some of the concentrated spent ammonia-water containing the sulphocyanides, so that the temperature of the retort is lowered and more ammonia is obtained. The gas is then washed or scrubbed with water, previously warmed to diminish its power of dissolving hydrocarbons and hydrogen sulphide. It is then passed through a weak acid or other substance capable of retaining the ammonia, and is then purified, as usual in gas-works, from cyanides, sulphocyanides, and a part of its hydrogen sulphide, leaving part of the latter purposely unabsorbed, as it is wanted afterwards. Now comes the operation interesting

us most here:—The gas is passed, at as low a temperature as possible (producing this by an air-cooler or freezing-machine, or else by the expansion of the gas after previously compressing it), through a hydrocarbon oil boiling at a high temperature. It then loses most of its illuminating-power, and is used as fuel for heating the retorts. In this process the H_2S previously left in is burned into SO_2. The products of combustion are brought into contact with ammonia-gas or ammonium carbonate, obtained by heating the ammoniacal liquor previously formed, whereby ammonium sulphite is produced, part of which is oxidized by the excess of air into sulphate. The inventor states that he thus obtained from one ton of coal, at a temperature of about 650° C., 16 gallons of tar, 37 gallons of ammoniacal water, 11 lb. of sulphur, 12½ cwt. coke, and 7000 cubic feet of gas, which gave 4 gallons of benzol testing 90 per cent. at 100° C. The gas can then be used for heating (for instance) the retorts, or it can be used for lighting by means of some "carburetting" process.

A detailed description of Davis's process, and an analysis of the crude benzol obtained, is found in the Journal of the Society of Chemical Industry, 1883, p. 522. He admits there that the loss of absorbing oil is greater than at first anticipated, and that the process will only pay with benzol at a certain price, which was then easily obtainable (4*s*. to 5*s*., or at least 3*s*. per gallon), but which is out of the question at the present time. It is also evident that such a lowering of prices, if it had not occurred from other causes, would have been the inevitable consequence of any large extension of the process. In the discussion on Davis's paper it was stated that it takes all the gas produced, and 1 cwt. of coke in addition per ton of coal, to heat the gas-retorts. There does not seem to be any prospect of this process being made to pay, so far as we can see.

E. Drew (B. P. 5039, 1883) proposed certain mechanical arrangements for treating the gas with heavy hydrocarbon oils. This patent has been made void; also another patent of the same inventor (No. 5505, 1883), in which it was proposed to treat the gas with such oils in a highly compressed state.

Levinstein (Journ. Soc. Chem. Ind. 1883, p. 217) points out that the quantity of benzol to be extracted from coal by these processes (carbonizing it for that special purpose, and condensing the benzol from the gas by oily absorbents) is 30 times the amount of that

yielded by coal in the ordinary process, namely allowing most of the benzol to remain in the gas, and only recovering what is found in the tar. The benzol obtained by the new processes, however, is not so easily nitrifiable as that made from tar.

While in the case of ordinary illuminating-gas it is a doubtful advantage to extract from it its most valuable light-giving constituent, benzene, and thus to greatly reduce its value, and while at the present time the carbonization of coal in such a way as to make the production of benzol the principal aim is utterly unremunerative, it seems a much more promising idea to submit the gases obtained *as a by-product in coke-making* (see further on) to a similar treatment for extracting the benzol, instead of burning the latter as fuel for the coke-ovens, along with the great bulk of those gases. It is evident that in this case the benzol may be considered a clear profit; for the gases are always far more than sufficient for heating the coke-ovens even after abstracting the benzol. This idea has been carried out by Carvès (B. P. 15920, 1884) for his own coke-ovens (compare later on)*. He employs as an absorbent for extracting the benzol from his waste gases the heavy portions of the oil that are obtained from the distillation of the tar obtained from his own ovens. The gas is first made to pass through scrubbers consisting of upright cylinders, filled with pebbles or ganister, over which the oil is made to flow down. From the scrubber the gas passes into one or more wash-boxes, the lower compartment of which is again charged with heavy oil, and communicates with an upper compartment by means of a great number of small tubes passing down from the partition and dipping into the oil, so that the gases entering above are caused, by pressure or by exhaust at the exit of the lower compartment, to pass down these tubes and to bubble up through the liquid. Several of these wash-boxes are employed in combination, and are so arranged that the oil flows downward from the first to the second, and so on to the last one, while the gases first enter the lowest and successively pass on to the highest wash-box, and thence to the ovens to be burned. The oil coming from the lowest box is further made to feed the above-mentioned scrubber, so that the gases richest in light hydrocarbons come into contact with the oil that has already taken up most of the hydrocarbons from the preceding gas, and the almost

* A patent for the same idea has also been taken out by J. Coates (B. P. 11202, 1885).

exhausted gas is always brought into contact with fresh oil. In order to separate the benzol from the heavy oil, the mixture is heated in a still provided with an external steam-coil, or heated from without by a fire or by coke-oven gas, to a point where the light oils are volatilized while the heavy oil is not affected. The escaping vapours are condensed in a worm in the usual manner; the heavy oil remaining behind is used over again in the wash-boxes and scrubber, as described above.

Attempts have also been made to extract the benzol from coal-gas in a different manner, namely by *passing the gas through nitric acid*, or a mixture of nitric and sulphuric acids. This was patented by Leigh as early as 1863, but nothing came of it. The process was once more taken up by J. A. Kendal (U.S. P. 252473, of 1882), who first passed the gas through strong sulphuric acid, in order to extract from it those hydrocarbons [belonging to the "unsaturated" fatty series] which form an impediment to the ready nitrification of the benzene, which latter was effected by a second passage through a mixture of nitric and sulphuric acids. It is not possible to avoid the formation of dinitrobenzene; and Kendal, from the first, sets out with the intention of producing this compound as the principal product. Evidently the process did not pay; and it was therefore modified in such a manner as rendered the previous removal of the unsaturated fatty hydrocarbons unnecessary (B. P. 1541, 1882). The coal-gas is passed through a superheater consisting of metal tubes partly filled with coke or charcoal and kept at a red heat. The flow of the gas is regulated by a valve or meter to the point at which most benzol is produced for a given weight of gas. This is ascertained by passing a trial quantity through a vessel containing a mixture of 1 part of strong nitric acid and 5 parts of strong sulphuric acid up to the point where the change of colour shows the mixture to be saturated with benzol. The dinitrobenzene formed is precipitated by water, dried, and weighed. This test is repeated till the best proportions for the given case are found. As an instance, good results were obtained by passing 8000 cubic feet of gas per hour through nine cast-iron pipes, 8 inches wide, and each exposed to the heat for a length of 10 feet. The superheating process reduces the illuminating value of the gas, but it is asserted to increase the quantity of benzol by from 5 to 40 per cent., and to make the gas fit for directly pro-

at Saarbrücken, all the gases and products of distillation being burned around the coking-chamber to heat it. From the description of the Pauwels-Dubochet ovens, which Oechelhäuser examined in 1860 during a visit to the La-Villette works of the Paris Gas Company*, it would appear that they had then been for some time in use for the production of excellent metallurgical coke, along with rather poor illuminating-gas, which was mixed with the richer gas made in ordinary gas-retorts. The temperature in those ovens was much lower than in the Knab ovens. Tar and ammonia must necessarily have been condensed, since the gas was required for illuminating-purposes; in fact, E. A. Behrens, who subsequently describes the same plant†, mentions that the yield of tar was 4·67 per cent., and that it was much lighter than retort-tar, also poorer in naphthalene and phenols. [The specific gravity (1·2) given for that tar is probably erroneous.] The Pauwels-Dubochet ovens seem to have been introduced merely on account of the higher value of the coke (at that time 35 frs. per ton, against 20 frs. for retort-coke), and seem to have been abandoned at La Villette for some time.

About the same time (in 1861) patents were taken out by Jones and by Blackwell for obtaining, by simple contrivances, tar and weak ammoniacal liquor when coking coal in pile. As might be anticipated, these attempts were not crowned with any success. Jones's plan has been described by Watson Smith ‡.

Knab's original furnaces only possessed bottom flues beneath their beds. A considerable improvement was effected by Carvès, under whose management 88 Knab ovens were erected at St. Etienne, which, however, were abolished later on. Carvès, at Commentry, first introduced the heating of the ovens by side flues in addition to the bottom flues. A description of those furnaces, as they were working in 1862, has been given by Gaultier de Chaubry§. The gases and vapours escaping from the closed coke-ovens were passed into a hydraulic main, cooled by air, where tar and ammonia condensed, while the gases were continually drawn off by exhausters, and employed for heating the coke-ovens, by issuing from an annular burner along with air admitted into its

* Dingler's Polyt. Journal, vol. clx. p. 394; Wagner's Jahresb. 1861, p. 674.
† Journ. f. prakt. Chemie, vol. ccvi. p. 277.
‡ Journ. Soc. Chem. Ind. 1884, p. 604.
§ Bulletin de la Société d'encouragement, 1862, p. 581.

inner space. In order to collect the condensable products more completely, the gas was first passed through coke-scrubbers fed with water, and then through a set of 500 upright lead pipes of ⅛ inch width, externally cooled by water. There were said to be obtained from 100 parts of coal :—

Large coke	70·00
Small coke	1·50
Breeze	2·50
Graphite	0·50
Tar	4·00
Ammoniacal liquor	9·00
Gas	10·58
Loss	1·92
	100·00

Barré, in 1863, mentions 7 tons of ammoniacal liquor and 5 tons of tar from 100 tons of coal.

The Knab-Carvès ovens were gradually introduced into other places. In the years 1866 to 1873, 53 such ovens were erected at Bessèges, and 100 ovens at Terre-Noire, near St. Etienne, in 1879.

The Bessèges coke-ovens have been minutely described by Dr. Angus Smith*, who, with very great foresight, warmly recommended this system at a time when hardly anybody in Great Britain had taken any notice of it.

Further attention was drawn to the Carvès ovens by Mr. H. Simon in a paper read to the Iron and Steel Institute in May 1880, but without making an immediate impression.

The Carvès ovens, as they were working at Bessèges in 1880, have been accurately described and figured in the 'Bulletin de la Société de l'Industrie Minérale,' † vol. ix. p. 283. After many trials they were made only 2 feet wide, to allow of the heat penetrating them thoroughly. Over a small fire-grate is placed the mouth of a pipe conducting the gases formed in coking, from which tar and ammonia have been abstracted, and here they are burned. The products formed in combustion pass underneath the hearth of the oven, then travel upwards to the topmost of the three flues built in the side-walls, and downwards through these flues into the

* Fourteenth and Fifteenth Reports on the Alkali Acts, for 1877 and 1878, pp. 49 *et seq.*

† Quoted through Dingler's Journal, vol. ccl. p. 254.

main flue leading to the chimney. The volatile products escape through a pipe from the interior of the coking-chamber; they first pass through a number of horizontal pipes, cooled by a stream of water, and then through scrubbers, where they are freed from tar and ammonia previously to being introduced into the combustion-chamber.

The most recent modifications of the Carvès ovens will be described subsequently.

Pernolet's coke-ovens* are very similar to Knab's. From Gurlt's description (*loc. cit.*) it would appear that they were made hotter than Knab's. The condensing-plant for tar and ammonia was added to them by Benut and Renant, and seems to have been very well constructed, but a very unfavourable account of the working of the ovens themselves is given by Stevenson†.

In 1873, H. Aitken, of Falkirk, conceived the idea of drawing off tar- and ammonia-vapours from beehive-ovens, and this idea was further developed in 1879‡.

In 1879, Ströhmer and Schultz (G. P. 8174) proposed drawing off the gases and vapours from coke-ovens by a sliding tube before they had time to be decomposed by the heat of the brickwork. Lest the quality of the coke should suffer by the gases being drawn off too fast, the sliding tube was raised or lowered by an automatic pressure-regulator. This plan was tried at Plauen, near Dresden, but without success.

In 1880 H. C. Bull patented an oven somewhat similar to Aitken's.

About that time Ed. Fischer constructed an oven for obtaining tar and ammonia from bituminous shale, and more particularly from the browncoal breeze found in enormous quantities in Bohemia in the shape of pit-heaps. The process is said to have answered well, but only yields an inferior coke, fit for heating domestic stoves§.

Up to the year 1881 none of the processes for obtaining tar and ammonia in coke-making had been found to be thoroughly successful, especially with respect to the quality of the coke, so

* Armengaud's 'Génie Industriel,' 1870, June, p. 281; Dingler's Journal, vol. cxcvii. p. 411.

† Journ. Soc. Chem. Ind. 1883, p. 604.

‡ Watson Smith, Journ. Soc. Chem. Ind. 1884, p. 604.

§ Hüssener, 'Stahl und Eisen,' 1883, p. 409.

that a prize offered in 1870 by the Berlin Society for the Advancement of Industry was allowed to lapse. The only exception to this rule, the Carvès oven, had not become sufficiently known outside a comparatively small circle. Whilst many different ovens were known which utilized the heat of the gases evolved, and indeed such ovens were very generally employed on the Continent, the further problem of recovering the tar and ammonia without in any way injuring the quality of the coke for blast-furnace purposes was tacitly or expressedly regarded as insoluble.

In 1881 the coke-making public in England and Germany almost suddenly became aware that the long-standing success of the Carvès oven was a reality, and that these ovens could even be improved upon. In England Mr. H. Simon, of Manchester, assiduously laboured for the introduction of Carvès' process, improved by a recuperator. We shall not here attempt to give a description of all the new coke-ovens patented during the last few years, more particularly since it would involve a corresponding number of diagrams; we shall merely give an enumeration of the different patents, along with a reference to the places where the descriptions are to be found, and we shall then select a few of the most important and most widely adopted plans for special description and illustration. We shall not give any account of such inventions as are only intended to utilize the coke-oven gases for heating-purposes, in order to increase the yield of coke.

Patents for coke-ovens with recovery of tar and ammonia have been latterly obtained by:—

Ströhmer and Schulz (G. P. 13395 and 16807).

H. Aitken (B. P. 2682, 1882).

U. Hegener (G. P. 13996).

Th. Hornig (G. P. 21908 and 23670).

F. Lürmann (G. P. 13021, 15512, 16134, 16741, 17055, 17179, 17203, 17661, 18128, 18927, 20205, 20211, 22602, 29088, 29557, 31660).

L. Semet and E. Solvay (G. P. 18935). Experiments made with their ovens by Ch. Demant are described in the 'Revue Universelle des Mines,' vol. xiii. p. 593; Wagner's 'Jahresbericht,' 1883, p. 1220.

G. Hoffman (G. P. 18795).

C. Otto and Co. (G. P. 13156, 16436, 16840, 19040, 20908,

24586, 31004, 31590, 34431, 37062, 37280). Their ovens will be described in detail below, as those most generally employed in Germany.

J. Jameson (B. P. 1947, 5076, and 5498, all of 1882; G. P. 24915, 25676, 27694). His coke-ovens are the most energetic attempts at combining the beehive-oven with a recovery of the by-products, and will be described below.

A. Hüssener (G. P. 16923, 20196).

H. Simon (as communicated by F. Carvès: B. P. 554, 1883; 15920, 1884).

H. Simon and Watson Smith (B. P. 4871, 1883).

H. Hutchinson (B. P. 2843, 1883).

O. Ruppert (G. P. 24404, 26307).

R. de Soldenhoff (G. P. 25824; B. P. 11967, 1885).

A. Klönne (G. P. 25673).

Hiltawski and Kahnert (G. P. 24438).

Schlesische Kohlen- und Kokeswerke in Gottesberg (G. P. 25825, 26421).

H. Herbertz (G. P. 15086, 17873, 25526, 27506, 31906, 34286).

Th. Bauer (G. P. 28530, 32235, 32660).

Th. Nicholson (B. P. 358, 1884).

C. E. Bell (B. P. 443, 1884).

J. McCulloch and Th. Reid (G. P. 31158).

A. M. Chambers and T. Smith (B. P. 4708, 1884; and B. P. 7358, 1885).

H. Stier (G. P. 26897, 35120).

F. Wittenberg (G. P. 26132).

A. Zwillinger (G. P. 29888).

Gebrüder Röchling (G. P. 33956, 35001).

Lothringer Eisenwerke at Ars (G. P. 32841).

J. Quaglio (G. P. 36357).

J. Schmalz (G. P. 37182).

Descriptions of most of these patents have been collected by F. Fischer in Dingler's Polyt. Journal, vol. ccxlviii. p. 249; vol. ccl. pp. 456 and 521; vol. cclii. pp. 253 and 283; vol. ccliii. p. 372; vol. cclvi. p. 359.

These are translated in the Journal of the Society of Chemical Industry, 1884, pp. 101, 505, 510, 531; 1885, p. 484.

A synoptic table of the ovens known up to 1884 has been given by Watson Smith, *eod. loco*, 1884, p. 605 (also in the Journal of

the Iron and Steel Institute of that year, with a table of diagrams and many further particulars).

Very important papers on many of these coke-ovens, with exact diagrams, have been given by A. Hüssener ('Stahl und Eisen,' 1883, p. 397) and C. Otto (*eod. loco*, 1884, p. 396).

We may with Watson Smith (to whose valuable contributions I am indebted for some of the following information) fitly class the various forms of recovery coke-ovens (as we shall style those ovens which aim at the recovery of tar and ammonia) as being derived, consciously or not, from three "root-forms," namely—first, the beehive, a sort of covered-in meiler or mound, into which air is admitted so that some of the coke is burned as fuel for the remainder; secondly, the Coppée oven; and, thirdly, the Knab-Carvès and Pauwels-Dubochet coke-ovens. The two latter belong to that class of coke-ovens which we may call horizontal closed ovens; both of them are so constructed that the gases evolved during dry distillation are utilized for heating the ovens from without, no air being admitted into the coking-chamber itself. The principal difference between the Coppée and Knab-Carvès ovens is as follows:—the former are provided with a large number of openings in the upper part of their side-walls, connected with an equal number of parallel heating-flues running perpendicularly downwards between each two ovens, and into these flues air is admitted, the flame ultimately passing below the sole. The Knab-Carvès ovens are heated by flues running horizontally in a zigzag form, also between each two ovens.

The upright ovens of the Appolt system have also been adapted to the recovery of tar &c.; but we shall not deal with these, as they do not seem to have been very widely used.

I. *Modified Beehive-Ovens.*

To the beehive form belong the meiler arrangements of Jones and of Blackwell, where tar and ammonia were collected by underground pipes, but the gases passed upwards by the central stack and were lost. Real beehive-ovens, modified for the recovery of tar and ammonia, are those of Aitken and of Jameson, which bear much resemblance to each other. Aitken blows air into his oven above the coke, along with the return-gas from the condensing and scrubbing apparatus, and he exhausts the gases and vapours, drawing them downwards through the bottom of the oven by

means of three perforated flues through which the gases and products pass, uniting in one main, before proceeding to the condensing-apparatus.

The special object of Jameson's invention (B. P. 1947 and 5076, 1882) was to utilize the existing beehive-ovens as much as possible, merely adapting them to the recovery of tar and ammonia. He places an exhaust-pipe with tap below the sole of his oven, and in addition to this he provides two other smaller pipes, through which the gases and vapours are returned at suitable intervals. The oven is filled as usual, and as soon as ignition has taken place above, the wider suction-pipe is caused to act gently, effecting a slow exhaustion of the by-products and gases. Since this process diminishes the quantity of the coke and makes it softer, Jameson returns through the other pipes a portion or the whole of the gas drawn off, and a portion or the whole of the tar-vapours to a similar oven, but one which has attained a further stage of combustion and ignition, in order that the carbon of the gases and vapours may become deposited in the pores of the coke thus treated, whilst the hydrogen burns at the surface of the mass or escapes. He claims various other possible modes of action and treatment of gas and by-products (such as the addition of pitch deprived of its valuable portions). →

Jameson further proposes (B. P. 5498, 1882) to treat carbonaceous or coaly matters, shales, &c., difficult or impossible to coke, such as "duff-coal" or pit-heaps, also on the partial-combustion principle in an oven which partakes of the nature of a reverberatory-furnace. It resembles a modified beehive-oven, with a fire-place and reverberatory-furnace fire-bridge attached, so that the flames from the furnace can play over the thick coking-mass on the deep-lying oven-bed, and then pass on to the chimney-flue, whilst the suction-process for gases and by-products is set up in the space below the perforated bed on which the coking-mass lies. He also proposes to adapt this process to the roasting of ores in order to recover by-products, and for the recovery of fairly pure carbonic acid from limestone or in sublimation.

Particulars about the working of the Jameson ovens are given by the inventor himself in the Journal of the Society of Chemical Industry, 1883, pp. 114, 228, and 405; and 1885, p. 314. He states a good many objections to the use of gas for heating coke-ovens from without, to which he prefers burning the surface coke,

by means of the downward suction employed. We will not enter into his theories, so many *facts* pointing the other way; his own ideas as to the use of the gas evolved in coking for other purposes were confessedly in an undeveloped state. The average yield per ton of coal is estimated by W. W. Pattinson at 10 lb. of sulphate of ammonia, 8 gallons of oil, and 12,000 cubic feet of gas. The cost of plant per oven, that is the addition of the new parts, varies from £10 to £20. The yield of coke is, "if anything, rather greater than in the ordinary oven," say 10 to 13 cwt. from one ton of Northumberland small coal, or 67½ to 70 per cent. from Durham coking-coal [in any case *very* much below that obtained with closed ovens of the Coppée or Carvès type].

In the paper read in 1885 (Journ. Soc. Chem. Ind. 1885, p. 314) Jameson discusses the reasons why his process, although it fell into the hands of the ablest of practical men, and was worked out in a great number of places, with no regard to expense, had not realized the anticipations of its inventors and its promoters. Modifications are described for making the oven-bottoms more nearly air-tight, and for cooling the gas in order to increase the yield of ammonia and oil.

We shall see further on that the *tar*, or rather (as Jameson himself calls it) the "oil," produced in the Jameson ovens is altogether different from gas-tar, being a low-temperature product, and is principally composed of paraffinoid hydrocarbons, such as exist in shale-oil, browncoal-tar, &c. But it is much less valuable than the latter; since its specific gravity is very high, there is very little chance of utilizing it for the manufacture of burning and lubricating oils, and the idea of "improving" it by passing it through red-hot tubes, as patented by C. E. Bell (B. P. 9510, 1884; extended to blast-furnace tar by B. P. 12681, 1884), and advocated by Armstrong (Journ. Soc. Chem. Ind. 1885, p. 451), is thoroughly impracticable, as will be shown later on. Hence the Jameson tar must be pronounced an object of very little value.

There is also no doubt that the yield of *ammonia* from the Jameson ovens is not very high, decidedly less than from closed coke-ovens. Obviously the admission of air is very prejudicial in that respect, although the low temperature of the Jameson oven ought to favour the formation of ammonia in other respects. It is also evident some of the ammonia is directly burned.

We will mention only one more attempt in a similar direction,

H. Hutchinson (B. P. 2843, 1883) believes is possible to obtain at will hard coke along with tar rich in benzol by causing a rapid rise in the temperature of ignition, or a soft coke along with tar rich in paraffin by slow coking. The former he proposes to effect by passing previously heated air through numerous channels or small flues into the ordinary coke-ovens, in order to hasten the coking and raise the temperature of ignition, the by-products being drawn off by flues in the upper part of the ovens. [That tar produced under such circumstances should be "rich in benzol" is very doubtful.] He also proposes producing heating-gas or illuminating-gas by passing, along with the air, superheated steam through a perforated tube rising in the centre of the oven amongst the fuel.

In any case we may here state it as an admitted fact: *that no coke-oven of the "open" kind, where air is admitted into the coking-chamber, yields tarry products similar to ordinary coal-tar—that is, such containing a considerable quantity of benzene, naphthalene, anthracene, and other aromatic hydrocarbons, employed as first materials in the manufacture of artificial dyes and colours.*

Some of the recovery-ovens retain the form of the *beehive, but so modified that the oven becomes a closed one,* no air being admitted into it, whilst tar and ammonia are evolved, all the heating being then done by the return-gas. This is the case with one of the ovens constructed by Pernolet, and also with that of Klönne (G. P. 25673). The latter draws off the gaseous products from the top and heats the sole of the oven by the return-gases remaining after condensation, till all the tar and ammonia are drawn off as far as possible. Then the second stage of the process is started by conducting the gases, instead of through the hydraulic main, into a vertical side-flue, some air being admitted at the same time in front of the lower part of the oven, and the partially burnt gases being completely burnt later on by air previously heated. This oven thus forms a connecting link between open and closed coke-ovens; it does not seem to have been employed to any great extent.

II. *Recovery-Ovens on the modified Coppée System.*

One of the most remarkable ovens of this class is *Lürmann's,* differing from all others in the continuous style of working adopted

in it*. The oven, which, like all other Coppée ovens, forms a narrow channel of moderate height and of considerable length (say 80 feet), consists for two thirds of its length of a heating- and coking-chamber, and for the last third of a storage-chamber. The front of the first chamber is closed by a door in the shape of a ram, moved alternately backwards and forwards. The coal to be charged falls down from a hopper in front of the ram, and is by this pushed into the oven, forcing on the charge already contained in the oven towards its other end, where the finished coke collects and is taken out by a discharging-apparatus. The gases and vapours pass away from the centre of the coking-chamber through a hydraulic main, and, after condensing the tar and ammonia, are used for heating the coking-chamber from without, the thickness of the walls being reduced to 2½ or 3 inches, the numerous partition-walls of the flues bracing them up to a sufficient extent. The whole is always under a considerable pressure, produced by the ram. The cooling of the walls during the charging and discharging, unavoidable in all other ovens, is done away with here; since the same quantity of coal is always in the same stage of distillation, the quantity and quality of the gas is invariably the same throughout the process; the details of the construction are such that a very high temperature can be maintained at will all over the coking-chamber. Owing to this and the high pressure, it has been found possible in the Lürmann oven to make hard smelting-coke from very dry, anthracite-like coal, the smalls of which are otherwise of hardly any use; but it is best to mix this with half its weight of ordinary coking-coal. It is not adapted to coking coal without the admixture of dry coal. It would seem from this description as if the Lürmann ovens were the most perfect of their kind, at least so far as the coking proper is concerned, and a goodly number of them have actually been erected in Westphalia; but they have not answered their purpose, and have been stopped, as the quality of the coke was not satisfactory and the discharging-apparatus showed serious drawbacks. Lürmann, in the discussion following the reading of the paper ('Stahl und Eisen,' 1883, p. 412), points out that his oven is not intended to compete with those destined for the ordinary descriptions of coking-coal; that it produces excellent coke from coal which is otherwise

* I take the description and criticism of this oven from Hüssener, 'Stahl und Eisen,' 1883, p. 401, where a good diagam is also given.

quite unfit for that purpose; that this coke is especially good for cupola-furnaces (as proved by certificates); and that his ovens yield tar and ammonia from coals otherwise useless for coking-purposes. It would not appear that the quantity and quality of the tar and ammonia recovered in Lürmann's ovens has been at all accurately ascertained, and we must therefore dismiss them for the present from our consideration.

Otto's first modifications of Coppée's oven for recovery purposes have been superseded by his later adoption of Hoffmann's principle, noticed below. We also refer the reader to the patent specifications and to the extracts in Dingler's Journal, and those given by Watson Smith, for the ovens patented by Herbertz, R. de Soldenhoff, and others, belonging to this class, none of which have met with an extensive application.

The most successful kind of oven, as regards the number introduced and the results obtained in Germany, is that originally patented by *Gust. Hoffmann* (G. P. 18795) and modified by *Dr. C. Otto & Co.* by a number of additional patents (comp. p. 43). The essential feature of this plan is a combination of Siemens's recuperators with the ordinary Coppée oven, provided with a number of improvements in details. In May 1886 there were 500 such ovens at work (110 in Silesia, 330 in Westphalia, 60 in Austria), each of them coking 1000 tons of coal, and producing 750 tons coke, 30 tons tar, and 10 tons sulphate of ammonia—exclusive of some descriptions of Silesian coal, which yield up to 17 tons of ammonium sulphate per 1000 tons of dry coal. The following is a description of these ovens, principally from the paper published by Otto in 'Stahl und Eisen,' 1884, p. 396, but with modifications to suit later patents; the diagrams are taken from the working drawings kindly lent to me by Dr. Otto.

Fig. 3 is a longitudinal section through the centre of an oven; fig. 4 a longitudinal section through the flues between each two ovens; fig. 5 a transverse section through a number of ovens; fig. 6 a plan of the condensing-apparatus. The letters show the same parts on all the diagrams.

These ovens are from 30 to 33 feet long, 2 feet wide, 5 feet 3 inches high to the abutment of the arch, with a 4-inch taper, and 2 feet 11⅛ inches from centre to centre. In lieu of the side openings through which, in ordinary Coppée ovens, the gases pass out of the coking-chamber down the sides and underneath

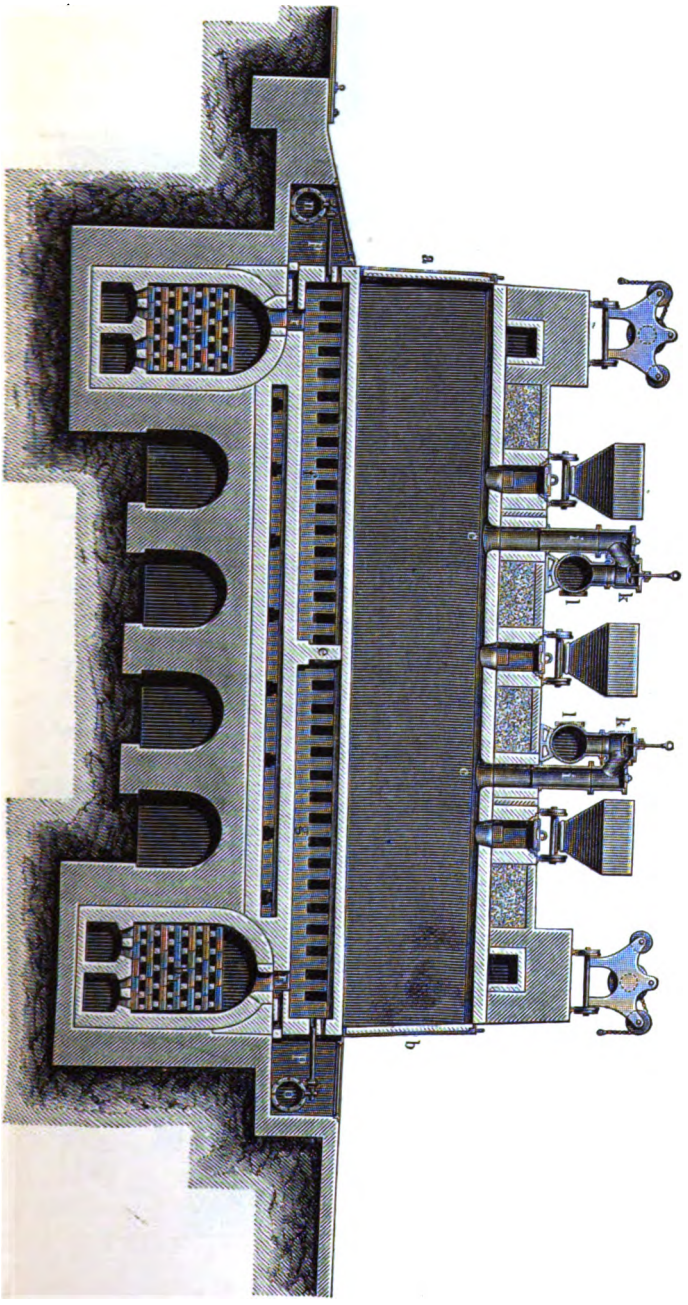


Fig. 3.

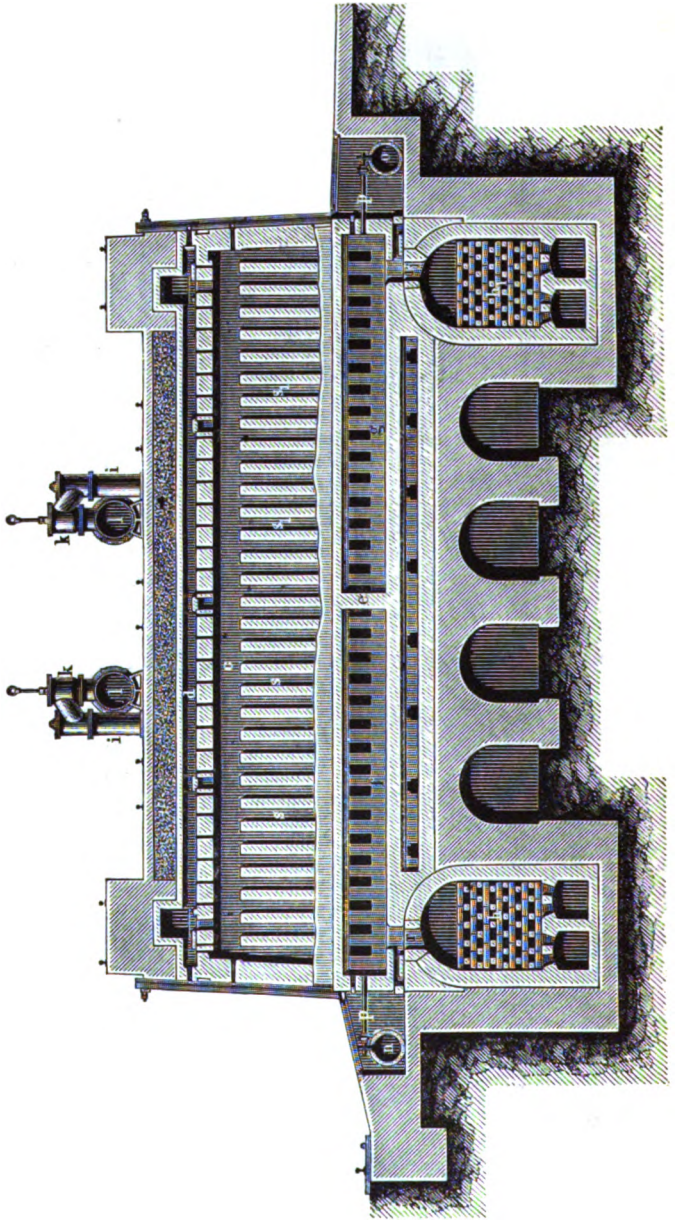


Fig. 4.

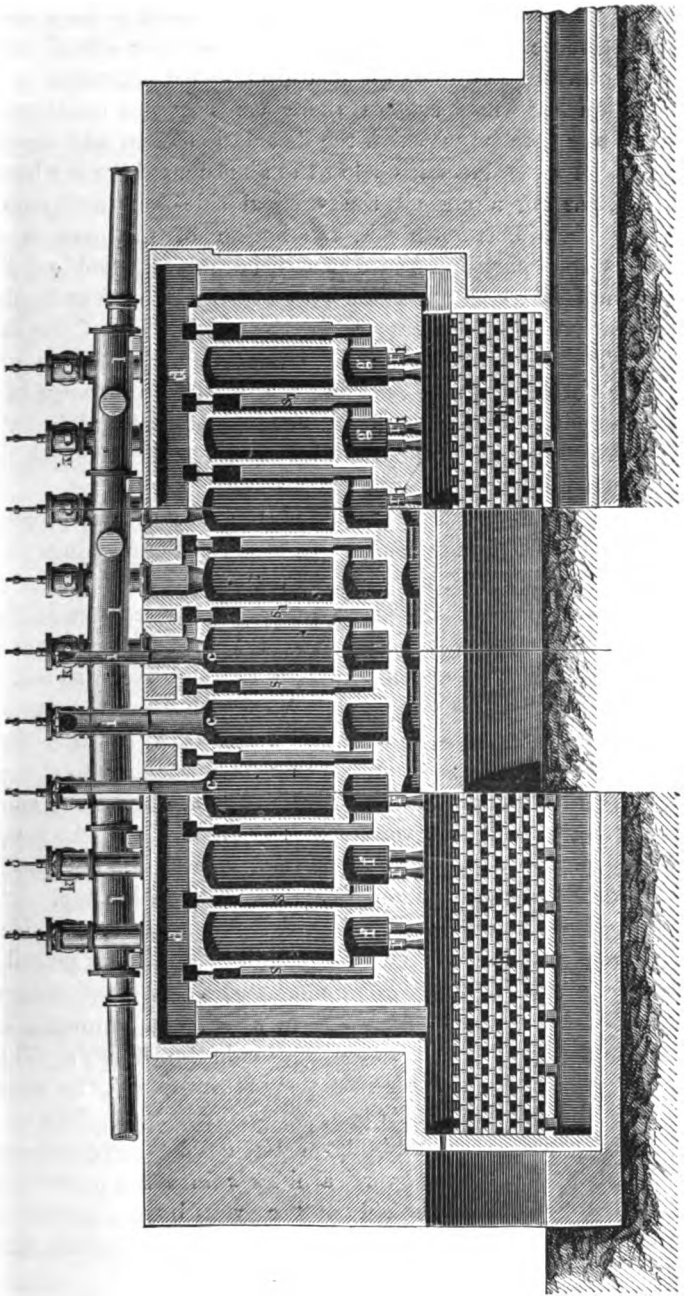


Fig. 5.

the bottom, in order to be burnt there, there is here no direct connection between the coking-chamber and the side of the oven; apart from the end doors for charging and discharging (*a* and *b*), closed during the operation, there are only two openings in the top arch, *c c*, through which the distillation gases and vapours can escape. In the side-walls below the abutment there is a horizontal flue *d*, passing along all the vertical side-flues and connecting them. Each bottom-flue in the length of the oven is divided midway by a partition *e* into two equal halves *f* and *g*. Each of these half-flues communicates with a recuperator, *h* or h_1, destined for heating the air necessary for the combustion of the heating-gas. The recuperators are long chambers, filled with an open network of bricks, and reaching along the whole range of ovens. At the end of the range the two recuperators *h* and h_1, by means of a throttle-valve, are made to communicate either with the fan-blast conducting air or with the chimney.

When the ovens are charged and the coking is in progress, the gases evolved from the coal escape through the openings *c c* in the oven-arches into the tubes *i i*, and then pass into the main receiver *l l*, the valves *k k* being left open. From the receiver *l l* the gases pass to the condensing-plant, where they are freed from tar and ammonia in the gas-coolers and in the scrubbers, as will be described below. The same exhauster which drew the gases to the condensing-apparatus now forces them back towards the ovens into the tube *m* (fig. 6), and from this, according to the position of the throttle-valve, either into the tube *n*, on the one side of the oven-range, or into the tube *o*, on the other side of the range. At each oven the tubes *n* or *o* communicate with the bottom-flue *f* or *g* by means of a small inlet-pipe *p* provided with a tap.

Suppose the gas is passed into the pipe *n*, on one side of the oven-range, the throttle-valve of the recuperators is placed so that the air (which is forced in by means of a fan-blast) enters at the same side into the recuperator *h*, which communicates opposite each oven, by openings *r r*, with the bottom-flue *f*. Thus both gas and heated air enter into the bottom-flue *f*, the combustion taking place partly in this flue, partly further on. The current of burning gases and very highly-heated combustion-products passes upwards by the parallel vertical flues *s* into the upper horizontal flue *c*, and on the other side of the ovens by the parallel vertical flues s_1 downwards into the bottom-flue *g*, from which the gases,

now completely burned, pass through the recuperator h_1 into the chimney, and on their way give up their heat to the network of bricks. After a certain time, say an hour, the throttle-valves are reversed, and the gaseous current now travels in the opposite direction: the return-gas from the condensing-plant enters into the tube *o*, the air into the recuperator h_1, the combustion takes place in the bottom-flue *g*, the products pass through the vertical flues s_1 upwards into *c*, and thence through the vertical flues *s* downwards into *f*, and at last through the recuperator *h* into the chimney.

Originally the plant was arranged in a different way, two parallel recuperators being arranged on each side, one for heating the gas and the other for heating the air. But the heating of the gas was not carried out from the first, and in the ovens subsequently built only one recuperator was provided, for the following reasons:—In the long chambers for heating the gas and air, separated by a partition, leakages might occur in that partition-wall, so that air and gas would get mixed and the brickwork might be fluxed. On each reversal of the throttle-valve a whole recuperator-full of gas would be lost, and this hot gas passing away to the chimney along with the contents of the hot-air recuperator might lead to an explosion. The volume of air required for combustion being six times that of the gas to be burned, it seemed preferable and less complicated to bring up the air alone to a very high temperature by the total heat of the combustion-products, instead of spending this partially for heating the gas. [This case is different from that of ordinary gas-producers, where the volume of the gas to be burnt, which has been produced by a partial combustion of the fuel, namely by the action of about half the necessary quantity of air on the fuel, is about the same as that of the air subsequently needed for effecting the total combustion.]

It cannot be denied that this modification has greatly simplified the Otto furnaces without impairing their efficiency. Dr. Otto points out that, owing to the slow conductivity for heat of fire-bricks, the air in Siemens's recuperators, worked alternately in opposite directions, is heated incomparably more quickly and highly than in those recuperators where the hot combustion-products travel on one side, the air to be heated on the other side of a brick partition, and the current of gases always flows in the

same direction *. In the Otto recuperators the temperature of the air rises to 1000° C., and the effect of this is that the cold gases, deprived of their tar, as they return from the condensing-plant, are far more than sufficient for carrying out the coking-process. If they were all to be burned, the ovens would get much too hot, and it is now (1886) found that there is an excess of 200 cubic metres (say 7000 cubic feet) of gas per oven per day which can be utilized in other ways. With a normal charge of 115 cwt. of dry coals per oven the coking-process is finished in 48 hours, but sometimes less, so that the quantity of gas must be diminished to bring the time up to 48 hours. Since both gas and air are blown in mechanically, it is quite easy to regulate the process at will.

The quality of the coke made in these ovens is altogether excellent; the yield considerably exceeds that formerly got from the same coal in Coppée ovens, without recovery of tar and ammonia. Calculated upon coal containing 10 per cent. water, it was formerly 61 per cent., and is now 68 per cent.; that is, upon dry coal, 67·7 and 75·56 per cent. respectively. Dr. Otto attributes this result to the absolute air-tightness of the ovens, along with a slight over-pressure. The temperature, as measured by a Steinle and Hartung's graphite pyrometer and controlled by the fusing of metallic alloys, was found to be 1200–1400° C. in the bottom-flue, 1100–1200° C. in the side-flues, 1000° in the recuperator at the time the air-current is admitted, and 720° when it is shut off, 420° in the chimney.

The *condensing-plant belonging to the Otto ovens* is shown in fig. 6. The gas is first passed through the tube *t* and cooled by upright wrought-iron cylinders or towers, A A. Within the cylinders are a number of iron tubes, fixed in partitions at top and bottom. The top partition forms a water-trough, constantly fed with cold water, which flows downwards through the tubes into the bottom box, and thence away into the next tower. The towers are so connected that the cooling-water used in one of them is taken up to a second tower, and so forth. The gas travels exactly in the opposite way in the space between the cooling-pipes, entering at the bottom and issuing at the top, and is thus cooled. The temperature of the gas in the tubes *i i*, rising from the ovens, is 600–700° C., in the main receiver, *l*, 200–400° (according to the distance from the tubes *i i*), in front of

* This is contradicted by Simon, comp. below.

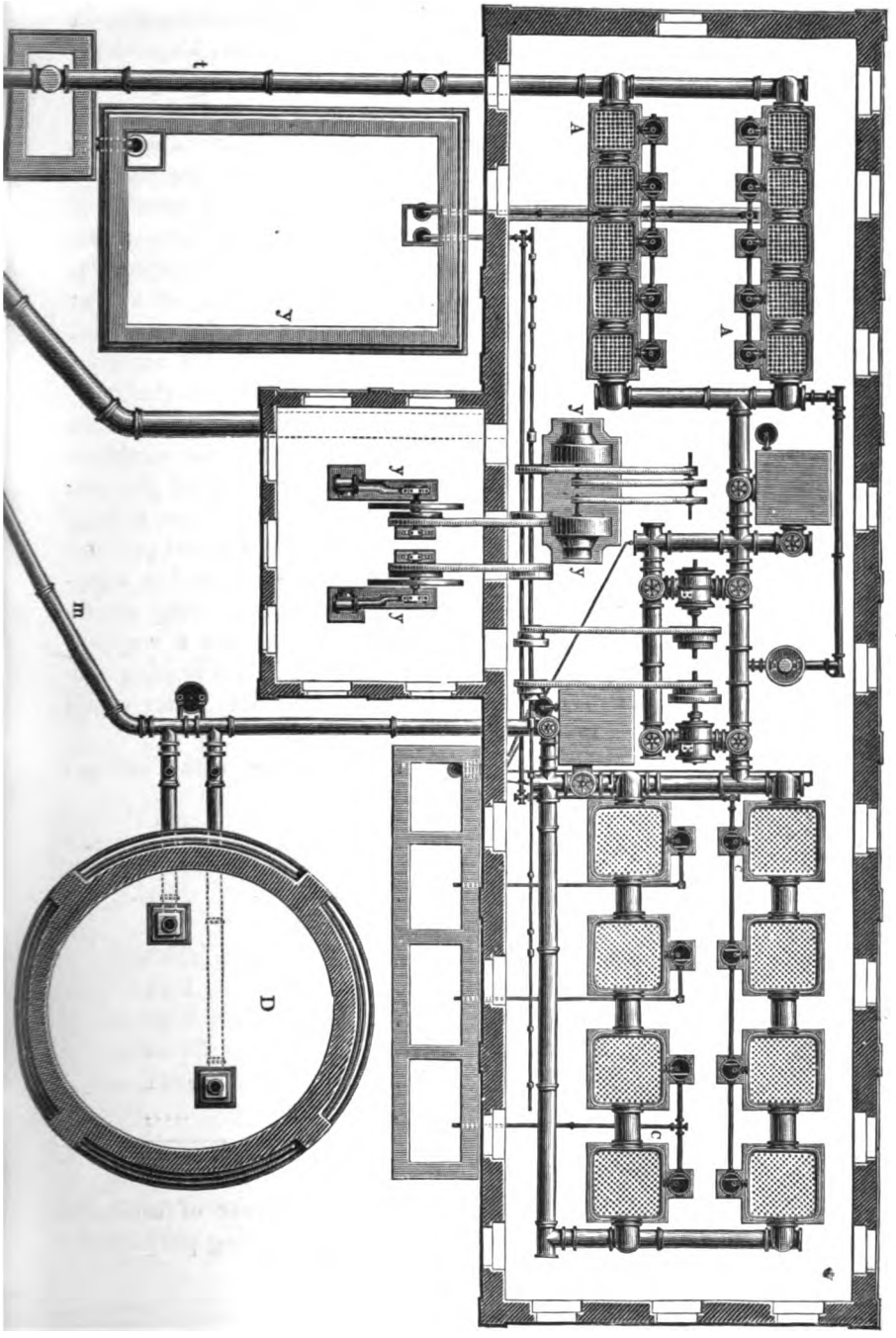


Fig. 6.

the gas-coolers 75–120°, after passing through them 17–30°. In the coolers A A it loses a good deal of its tar and about 75 per cent. of its ammonia, in the shape of ammoniacal liquor. The quantity of cooling-water required is about 5 tons per oven in 24 hours.

The gas is aspirated from the coolers A A by means of blowers B B, and is forced into the scrubbers C C. These are upright wrought-iron cylinders or towers, containing a large number of perforated iron shelves, 4 inches apart; water trickles down through these, whilst the gas travels from the bottom upwards. The ammonia is thus washed out; the liquor runs off at the bottom, and is, in case of need, pumped up over and over again, till it is strong enough for sale. Several scrubbers are connected in such a way that the gas at first passes through that containing the strongest liquor, and at last that fed with fresh water. Along with the remaining 25 per cent. of ammonia, the scrubbers also produce a good deal of tar. The temperature of the gas, which is now returned to the ovens, is 13° C. Since a large quantity of gas cannot be burned in the ovens, as it would produce too much heat (as mentioned above), the excess is stored in a gas-holder D, and can be used for illuminating, for heating steam-boilers, or other purposes. The gas-holder also acts a very important part in equalizing the pressure, and in preventing any damage from chance explosions, in which case only water would be driven out from underneath the gas-holder.

The composition of this gas in a special case (the Pluto-pit ovens) was :—

	Moist. per cent. by vol.	Dry. per cent. by vol.
Benzene vapours, C_6H_6.....	0·60	0·61
Ethylene, C_2H_4.....	1·61	1·63
Sulphuretted hydrogen, H_2S .	0·42	0·43
Carbon dioxide, CO_2.....	1·39	1·41
Carbon monoxide, CO	6·41	6·49
Hydrogen, H.....	52·69	53·32
Methane, CH_4	35·67	36·11
Water	1·21	.....
	100·00	100·00

Such gas has about half the illuminating-power of ordinary, retort-made coal-gas, and it can be used for lighting purposes by

employing sufficiently large burners. In Westphalia it is employed for heating steam-boilers, along with the waste heat of the gases issuing from the recuperators into the chimney (420° C.).

Tar and *ammoniacal liquor* are separated by settling in large tanks. If the liquor is not strong enough for sale or for working up in the distilling-apparatus, it is used over again in the scrubbers till it comes up to 4° or 5° Twaddell, when it contains about 1·7 to 1·8 per cent. NH_3. Westphalian coal yields about 14 per cent. of liquor at 4°, equivalent to a yield of 1 ton of sulphate of ammonia per 100 tons of dry coal. In the Saarbrücken district the yield is only 14 to 16 cwt., in Lower Silesia 16 to 18 cwt., in Upper Silesia 26 up to 34 cwt. per 100 tons of coal.

The yield of *tar* differs a good deal, according to the quality of the coal and to the efficiency of the cooling-apparatus; it may vary from 2 to 3½ tons per 100 tons of coal.

The following analyses were made in April 1886 of tar obtained from the same coal (A in a gas-works in ordinary retorts, B from a set of Otto's coke-ovens) :—

	A. Gas-tar.	B. Coke-oven tar.	
Water.....	2·9	2·2	per cent.
Light oil up to 200°	4·0	3·4	,,
Benzol for aniline...	0·92	1·1	,,
Solvent naphtha ...	0·20	0·32	,,
Creosote oil	8·6	14·5	,,
Crude naphthalene .	7·4	6·7	,,
Anthracene oil	17·4	27·3	,,
Pure anthracene ...	0·60	0·70	,,
Pitch	58·4	44·3	,,
Carbon	15–25	5–8	,,

These comparative analyses show a decided superiority of the tar from Otto's ovens over the gas-tar; but more material is required for deciding this point.

The expenses of recovering the tar and ammonia are not considerable; they consist principally of the cost of pumping the (rather large) quantity of cooling-water, the ammoniacal liquor, &c.; the cost of labour and repairs is very slight.

The following figures concerning the cost of erecting and working the Otto ovens have been supplied to the author by the inventor. The cost of erection naturally varies a good deal

according to the situation. On an average it may be taken as Marks 3050 (say £150) per oven for the ovens themselves, and Marks 6000 (not quite £300) per oven for the very extensive condensing-plant, gasholder, Feldmann's apparatus for ammonium sulphate, &c. This also includes duplicate engines, pumps, and exhausters, and substantial buildings for all these erections.

A battery of 60 ovens converted in 6 months' time 3073 truck-loads of 10 tons of coal each into coke, and yielded at the same time

	Per 100 kilog.	
915,245 kilog. tar (say 3 per cent.)	at M. 2·30 = M. 21,050·63	
313,446 kilog. ammonium sulphate (1·02 per cent.) at M. 23 =	72,092·58	
		M. 93,143·21
Deduct Sulphuric acid 313,446 kilog. at 3·80 = M. 11,910·95		
„ Wages	9,326·26	
„ Salaries	2,936·97	
„ Sundry materials	2,571·50	
		26,745·68
Leaving per 6 months a profit on tar and ammonia ... = M.		66,397·53
„ „ 12 „ ditto ditto ... M.		132,795·06
Or, say,		£6,600.

That is to say, each oven has coked per annum 1020 tons of coal, and the extra profit on tar and ammonia per ton of coal has been M. 2·16 (say 2*s.* 9*d.*).

III. *Recovery-Ovens on the Modified Carvès System.*

In the introductory part of this chapter (pp. 40 & 41) we have spoken of the former stages of this process, namely of Knab's, Carvès', Pauwels-Dubochet's, and Pernolet's ovens. Since attention was drawn to the undoubted success of Carvès' ovens, first by Angus Smith, then by H. Simon and others, there have been quite a number of "modifications" of the Carvès ovens, as Hüssener's, Carvès' own (generally called the Simon-Carvès oven), Ruppert's, Semet and Solvay's, Seibel's, the Gottesberg Coal and Coke Company's (compare list of patents, pp. 43 & 44).

Most of these systems have only met with a very restricted application, and we shall confine our description to those two which have been more widely introduced, namely Hüssener's and the "Simon-Carvès" oven, both of them (like some of the others) based upon a previous heating of the air required for combustion—a feature which we have also seen to be the essential point of the Hoffmann-Otto system.

Fig. 7.

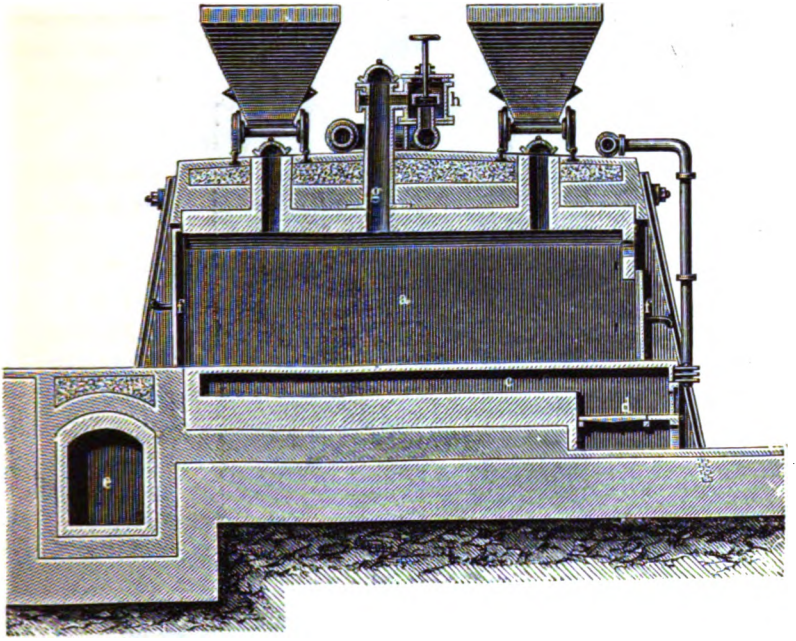


Fig. 8.

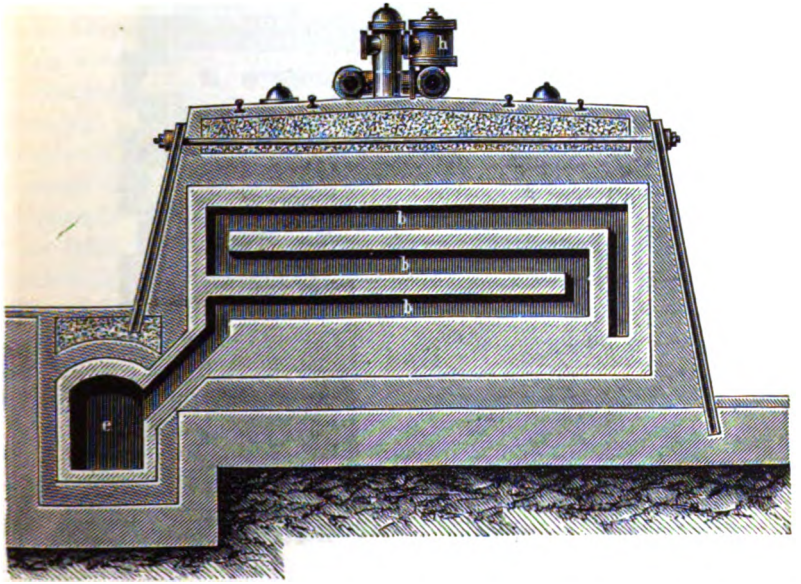


Fig. 9.

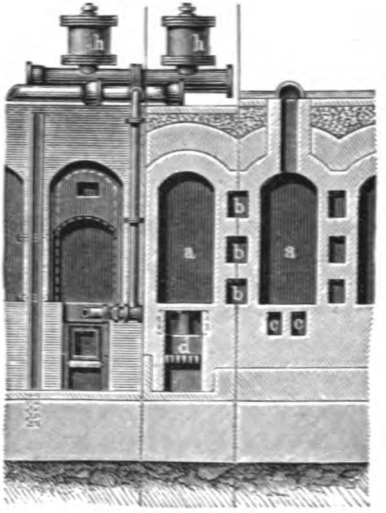


Fig. 10.

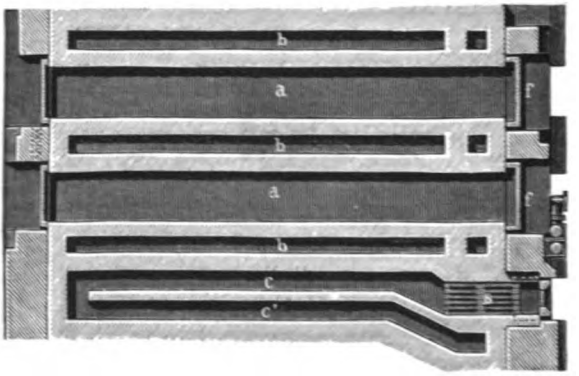
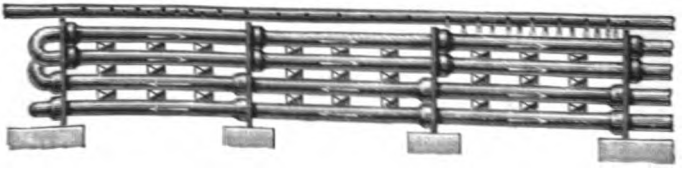


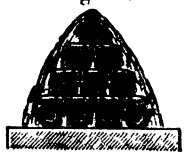
Fig. 11.



The following is a description of the original Carvès ovens, as they have been working in the east of France for a long time (comp. p. 40). These ovens are shown in figs. 7 to 10; fig. 7 is a longitudinal section through the centre of the ovens, fig. 8 the same through the flues, fig. 9 a cross section, fig. 10 a sectional plan. A number of ovens are grouped side by side, each forming a long, narrow chamber *a*, of rather more than a man's height, horizontal zigzag flues (*b b b*) being formed both in the partition-walls and (*c c*) under the floor of each oven. At one end of the bottom-flue there is a small fire-place *d*, consisting of a fire-grate and ash-pit with suitable door, the fire-door having fitted above it a nozzle, through which gas produced in coking is admitted, to form a flame over some fuel burning in the grate. Very little fuel is used here, consisting of refuse coke, merely in order to keep the gas ignited, and the grates are only charged twice every 24 hours.

The products of combustion pass from the fireplace *d* along a flue *c*, under the oven-floor, to the end farthest from the fire, and return along another flue *c'* under the floor to the fire-end; they then ascend by a flue in the partition-wall to the uppermost of the three horizontal flues, *b b b*, and descend in a zigzag direction along these flues, finally passing into a horizontal channel *e* leading to a chimney. Thus the oven is heated at the bottom and the sides, no air being allowed to enter the ovens, and no coke being burned within them. The ovens are fed from the top, the coal is evenly distributed by rakes introduced at end openings provided with doors, *f f*, tightly luted while the oven is in operation; through these, at the end, the coke is pushed out by a mechanical ram. Through the middle of the roof rises a gas-pipe *g* provided with a hydraulic valve *h*, which closes the passage by a lip projecting down from it into an annular cavity surrounding its seating, in which it is immersed in a quantity of tar and ammoniacal liquor collected there during previous distillations. The volatile products of the coal distillation rise by the gas-pipe *g*, and are led through a range of pipes (fig. 11) kept cool by external wetting; so that the tar and ammoniacal liquor become condensed and separated from the combustible gases. The cooling-pipes are arranged in pyramidal form (fig. 12), surmounted by a water-pipe having numerous holes. The gas is

Fig. 12.



further passed through scrubbers moistened with water, where more ammoniacal liquor is formed, which is repeatedly used in the scrubbers till it reaches saturation. The gas, having been deprived of all valuable by-products, is led by pipes to the nozzles at the fireplaces under the sole of the ovens, where it is burned. The movement of the gases from the ovens, through the condensers and scrubbers, and back to the fireplaces is caused by a Beale's exhauster, similar to those used in gas-works.

The pushing out of the finished charge by means of the steam-ram, which can be brought opposite each oven, and the refilling from the trucks ready on rails over the charging-holes, need not take more than from 10 to 15 minutes.

The drawn-out coke is quenched as usual, and is found even superior in quality to that produced in beehive-ovens, especially since the ovens have been more and more narrowed (now to 2 feet width). In fact the hardness of the coke increases as the width of the oven (that is, the thickness of the layer of coal treated) decreases, owing to the more intense heat to which the coal or coke is subjected. [In this respect the Carvès and Coppée ovens show exactly the same results, as might be expected from their similarity in principle.] In the two-feet ovens a charge is finished every 48 hours.

The Carvès ovens produce 75 per cent. of coke from the same coal which in beehive-ovens would yield at most 65 per cent. Besides this, and the recovery of the tar and ammonia, the waste heat of the ovens suffices for producing steam to the extent of 45 lb. and of 4½ atmospheres per hour and per ton of coal coked. At Bessèges all the machinery required in the manufacture of coke and its by-products is now driven by steam raised in this way, and a large surplus is left for other purposes; a battery of 100 ovens will furnish steam for about 400 horse-power over and above the making of the coke and the separating of the by-products. [We have seen, p. 56, that a very large surplus heat is also furnished by the Coppée ovens as modified by the Hoffmann-Otto process.] The coke produced in the Carvès ovens has not the same white silvery appearance nor the same long columnar structure as that obtained from the beehive-ovens, but is rather grey in colour and shorter in structure; it is, however, quite as dense and hard.

The last battery of a hundred ovens erected at Terrenoire cost

about £15,000*, with all machinery and apparatus for collecting the by-products, rail-connections, coke-platforms, &c.; in England the cost would have been considerably less. Each oven is 6 metres × 0·75 × 1·70, or 19 feet $8\frac{3}{16}$ inches long × 2 feet 6 inches wide × 5 feet 7 inches high; they take a charge of 5 tons of coal, which is finished within from 60 to 72 hours, so that coke is produced at the rate of from 1100 to 1400 kilos. (=22 to 28 cwt.) per 24 hours per oven, or at least 360 tons of coke per annum.

The cost of repairs, if the oven has been substantially constructed, is exceedingly small. The number of workmen employed on a battery of 100 ovens, producing over 100 tons of coke per day, is 48, including two foremen and two masons for repairs. The daily wages at Terrenoire are 184½ francs, say 1*s.* 6*d.* per ton of coke; the total cost of producing the coke at Bessèges is about 3 francs (or 2*s.* 6*d.*) per ton, including labour, repairs, &c. The principal advantages claimed are: greater yield of coke by fully 10 per cent., and a yield of about 4*s.* worth of useful by-products [this figure would be very much smaller at present prices of tar and ammonia]; also an almost entire absence of smoke or noxious vapours.

The practical results obtained with a set of 25 Carvès ovens at Messrs. Pease's collieries, near Crook, in the County of Durham, have been described by Mr. Robert Dixon (Journ. Iron and Steel Institute, No. ii., 1883; abstract in Journ. Soc. Chem. Ind. 1883, p. 404).

The ovens are 23 feet × 6 feet 6 inches × 19½ inches, containing a charge of 4½ tons of coal to each oven. They are connected along the top by a 10-inch gas-pipe, with a valve-box to each oven. The gas is drawn from the ovens by a Beale's patent exhauster, 2 feet 3 inches in diameter, and capable of drawing 30,000 feet of gas per hour, at 80 revolutions per minute, a 3 H.P. engine being sufficient to drive it. The fuel for the traversing steam-ram used for forcing the coke out of the ovens amounts to 28 lb. per oven. The condensing-arrangement consists of 10 rows of 10-inch metal pipes in serpentine form, the length of each row being 32 feet, and above them a perforated 4-inch pipe for the spray of water, which consumes 1000 gallons of water per hour; also three cylindrical iron gas-scrubbers, 13½ feet high and 6½ feet wide, con-

* This seems remarkably little, and is stated without vouching for the correctness of the amount; comp. Hüssener's ovens.

nected to each other with 8-inch metal pipes, and two large metal washing-boxes.

The whole of the bricks and fireclay lumps required to be placed in any important position were carefully dressed and faced with the chisel, in order that every joint should be perfectly gas-tight, and the ovens in fact show no signs of wear and tear. The cost of the 25 ovens was as follows :—

	£	s.	d.
For bricks, lime, &c.....	1300	8	4
Labour	1517	16	10
Sundries.....	276	17	10
Ironwork	1129	19	4
Steam-ram	472	0	0
Three gas-scrubbers	115	0	0
Gas-exhauster	247	10	0
Six liquor-tanks.....	500	0	0
Two steam-pumps for liquor and tar .	101	0	0
	£5660	12	4

Equal to £226 8*s*. 6*d*. per oven (N.B. *without* recuperators).

The cost of an additional block of 25 ovens is estimated at only £3973 15*s*. 6*d*., as most of the gas machinery is equal to the working of 50 ovens; the total cost of 50 ovens thus being brought up to £9634 7*s*. 10*d*., or £192 13*s*. 9*d*. per oven; for 100 ovens, the average cost per oven would be £172 2*s*. 2*d*.; but these estimates do not include patent rights or tools (beehive-ovens, built on the same rate, would cost £57 10*s*. 9*d*. per oven).

The result of working the battery of 25 ovens over 215 days has been that one ton of coal produced 77·03 per cent. of good coke, that is 15 per cent. more than with ordinary beehive-ovens; also 6·12 gallons of tar and 27·70 gallons of ammoniacal liquor at 7 or 8 degrees Twaddell. The cost of coke-burning, including all labour connected with obtaining the by-products, was 2*s*. 3·96*d*. per ton of coke, or 1*s*. 3·31*d*. in excess of the cost in beehive-ovens, without recovery of tar and ammonia. The appearance of the coke generally differs from the beehive coke; it usually lacks the silvery brightness * and columnar structure of the latter; it is more in the form of large circular blocks of great strength and

* The coke produced from Staffordshire coal in these ovens, however, possesses this silvery brightness, and is accepted as in every respect equal to other blast-furnace cokes (Watson Smith).

density, and less liable to break in filling, in transit, or in tapping. Although there is some prejudice against it on account of the external difference, it is in reality all that can be desired for blast-furnace or foundry purposes.

The only trouble occurring with the Carvès ovens arises from the highly bituminous character of the Pease's West-coal, which causes pitch to be collected in the valve-boxes and gas-mains; but this can be avoided by constructing these on a different plan. Care must also be exercised to keep at all times a slight pressure of gas within the ovens, so as to prevent the danger of drawing air into them, and thus causing an explosion; for this purpose the engineman must carefully watch the water-gauge placed on the gas-main between the ovens and the exhauster, and frequently examine the four screw-plugs placed at various points in the gas-mains on the top of the ovens; when these are opened, the gas should slightly blow out and no air should be drawn in. If, on the other hand, the inside pressure becomes too great, the speed of the exhauster being too slow, the pressure of gas may spring the metal doors at each end of the ovens and break the luting which surrounds them, whereby a large quantity of gas will escape.

These coke-ovens, before they can be put to work on gas, must be brought up to a much higher temperature than is required for beehive-ovens; and the drying and heating must be done very carefully, as they are built of large fireclay lumps, and much damage might be done by excessive firing at the commencement.

Each charge takes from 60 to 72 hours; but this time could be reduced to 48 hours by introducing the recuperators and otherwise conforming to the French system of working the ovens.

The Carvès ovens have been considerably improved by the introduction of recuperators, patented in 1883 (No. 554) by Henry Simon as a communication from François Carvès*. Figs. 13 to 17 show the arrangement. Fig. 13 is a longitudinal section through a coking-chamber and cross section through the external air and smoke-flues on line $a\,\beta$, fig. 15. Fig. 14 is a longitudinal section through the partition-wall of the coking-chambers on line $\gamma\,\delta$, fig. 15. Fig. 15 is a part plan and part sectional plan of the coking-chambers and flues. Fig. 16 is part front elevation and part cross section; fig. 17 a sectional plan to a smaller scale of the

* I take the diagrams in the text partly from the patent, partly from detailed unpublished drawings, supplied to me by the kindness of Mr. Henry Simon.

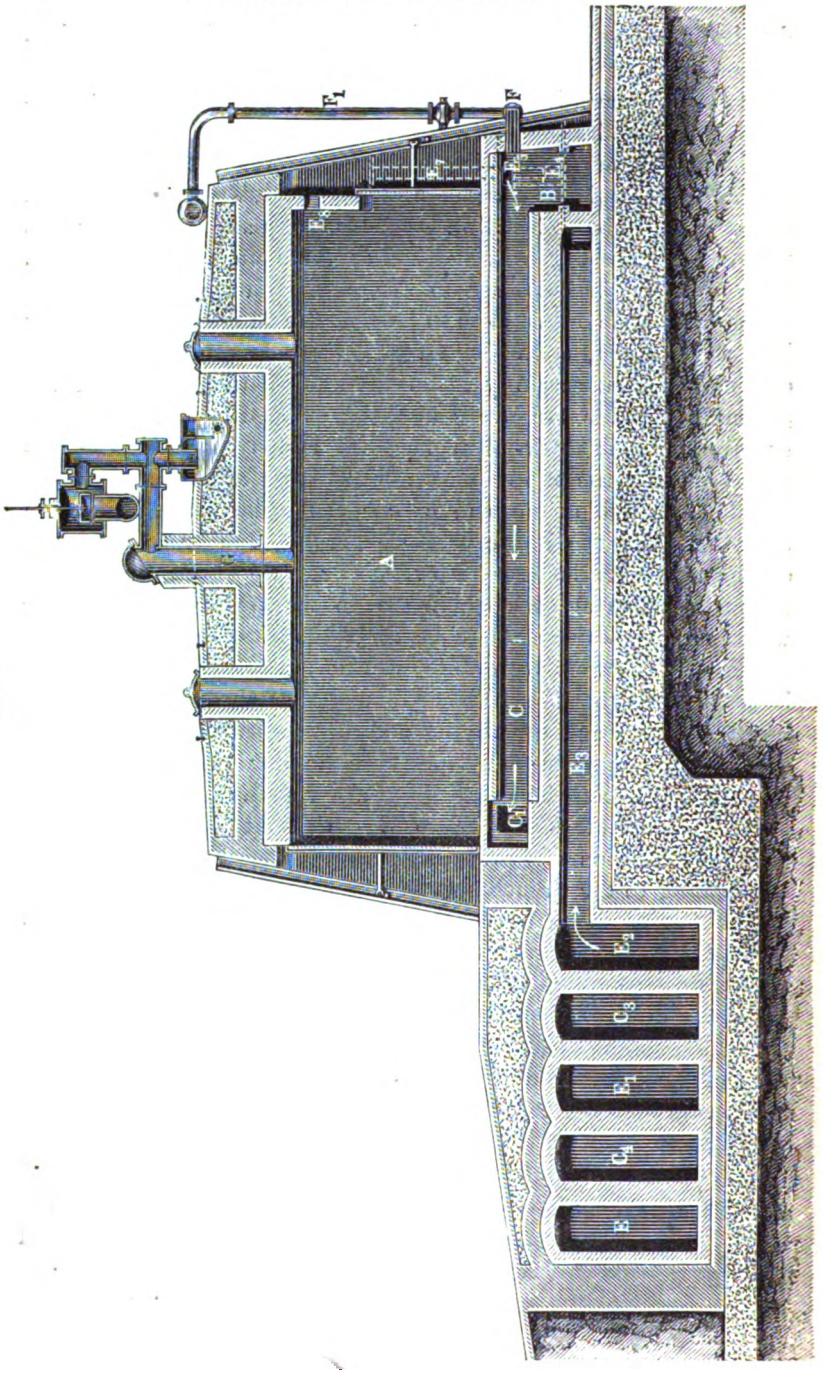


Fig. 13.

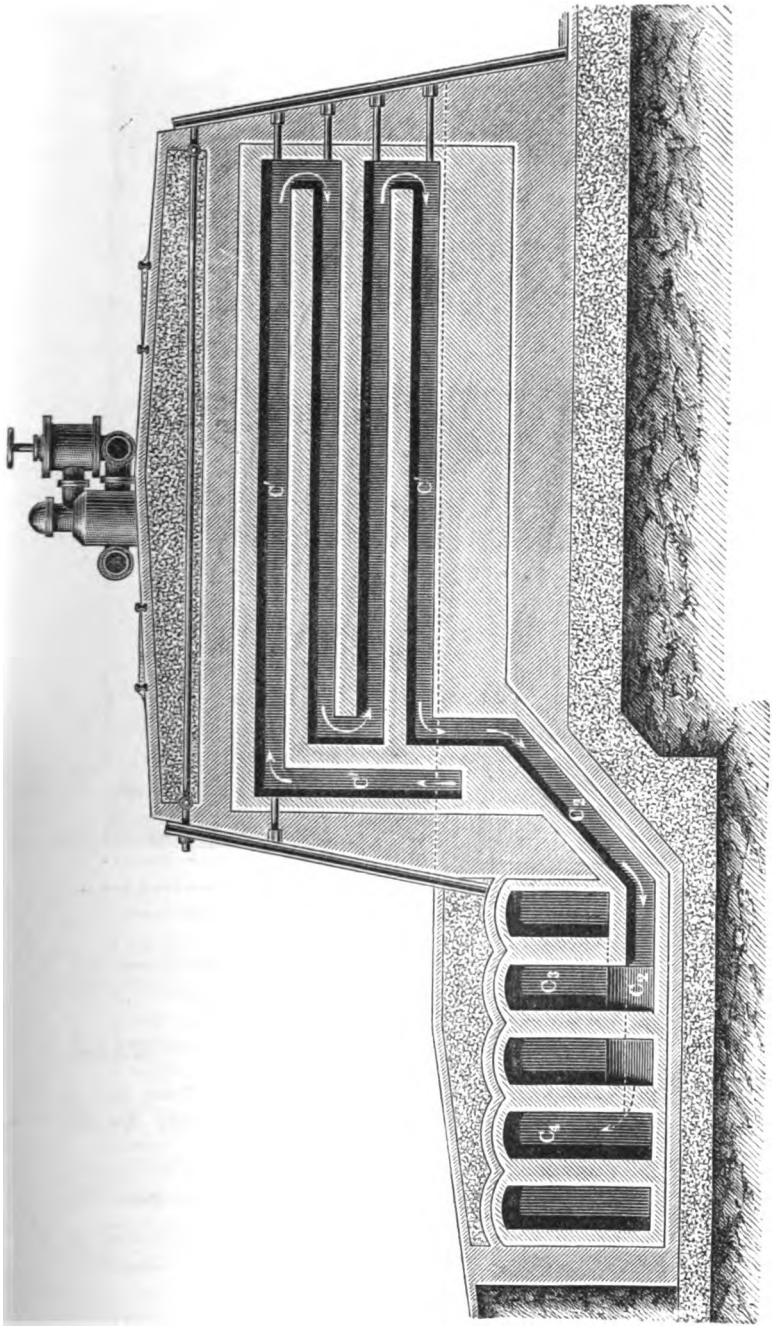


Fig. 14.

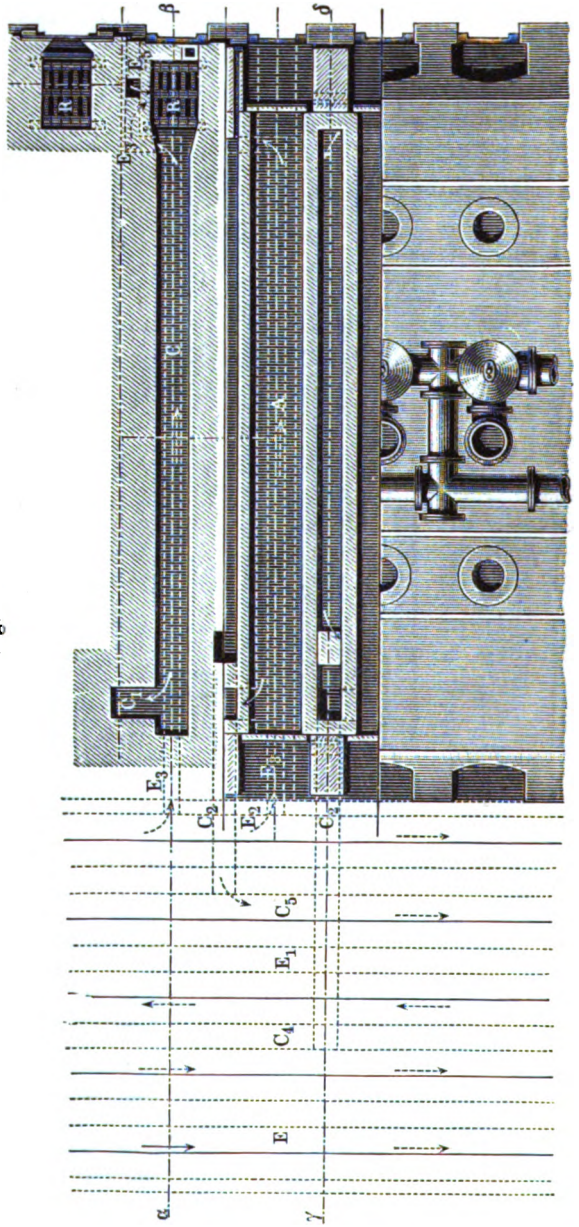


Fig. 15.

Fig. 16.

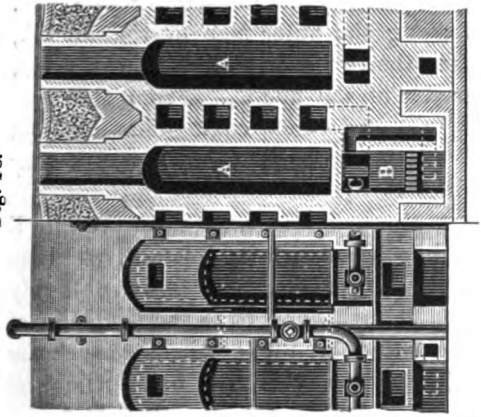
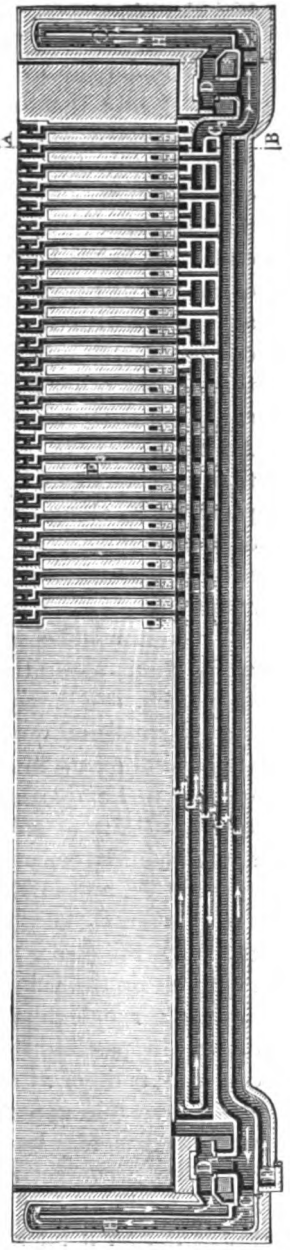


Fig. 17.



smoke-flues and air-heating flues. We notice the coking-chambers A A (18 to 20 inches wide), the fireplace B with flue C leading thence under the oven-floor to the opposite end, where it passes laterally into the flue C_1 in the side wall of the chamber, first rising to the upper part of the wall, then descending in a zigzag direction (fig. 14), and then down the inclined flue C_2 into the external smoke-flues C_3 C_4. These flues, as will be seen from the plan, fig. 17, extend along the whole range of the coking-chambers, each flue being closed at one end and communicating with the chimneys D D_1 at the other end. The flues C_1 communicate alternately with the flues C_3 C_4, so that the combustion-gases of one half of the range of ovens are discharged into the flue C_3 and those of the other half into C_4, the flow of such gases towards the chimneys D D_1 taking place in contrary directions in the two flues. An air-flue E extends first along the outer side of the flue C_4, then runs along at E_1 between the two flues, and, again returning, passes at E_2 along the other side of the flue C_3. From this part of the air-flue, branches E_3 pass off to each coking-chamber, and extend beneath the flue C to the fireplace B, with which they communicate through openings E_4 E_5.

Thus it will be seen that atmospheric air, entering the flue E at E_6, passes along the same in contact with the hot walls of both C_4 and C_3, and lastly through E_2, whence it passes in a highly heated condition through the branch-flues E_3 to the fireplaces of the several ovens, in order to enter there into combustion with the gaseous fuel employed, which, in some cases, may be kept ignited by a small fire of solid fuel on the grate shown at B. In E the air flows in the contrary direction to the current of the combustion-gases in C_4, and in E_1 it flows in the contrary direction to that of the gases in C_3, so that the coldest air in each case comes in contact with the cooler part of the smoke-flues, and thus the heat is taken up by the air in the most effective manner. As the air, in passing through the flue E E_1, becomes heated to a considerable degree, in passing through the flue E_2 (which is to a very slight extent in contact with the brickwork of the oven) it will not absorb any appreciable amount of heat therefrom, and even this absorption, small as it is, may be entirely avoided by arranging the flues so as not to be in contact with the brickwork of the oven, except where they enter it.

The hot air is made to enter the fireplace through the openings

E_4 and E_5, the latter being in close proximity to the inlet nozzle F for combustible gas, supplied through the pipe F_1; while the opening E_4 serves to supply air when required to the before-mentioned small fire on the grate. The hot-air flue is also by preference extended up in the front wall of the ovens, as indicated at E_7, in order to communicate at E_8, or at any other convenient point, with the upper part of the flue C_1, so that a portion of the hot air entering there may effect the combustion of any unconsumed combustible gases that may have passed away from the fireplace. The combustible gaseous constituents distilled off from the ovens escape through the flue G, and are led through proper pipes or hydraulic mains to any suitable known apparatus for condensing the tar and removing from the gas other condensible and useful constituents; and the gas, after such purification, is then utilized in whole or in part as fuel for heating the coke-ovens, for which purpose it may either be led directly to the fireplace B, through the pipe F_1 and nozzle F, or it may also be previously heated by first passing it through a pipe or flue situated within or close to the smoke-flues C_4C_3. As, however, the quantity of gas consumed is small in proportion to the air-supply, the advantage gained in heating it is in most cases not sufficiently great to justify the additional expenditure and greater complication caused by providing apparatus for heating it.

As shown at fig. 17, the combustion-gases may, before escaping up the chimneys D, be made to pass through the flues H of steam-boilers or of ovens or kilns or evaporating-pans, in order still further to utilize their heat.

The patent also comprises another modification, in which there is only one external smoke-flue, into which the flues of all the ovens open, and on each side of which there is an air-flue so arranged that the external air passes in the contrary direction to the current of the combustion-gases. In a further modification, instead of having separate air-supply and smoke-flues, the same flues are made to serve alternately for taking up the heat from the combustion-gases and imparting such heat to the air-supply, as in the well-known Siemens's recuperators (such as Hoffmann and Otto employ with the Coppée ovens).

The inventor lays special stress upon his arranging the recuperator-flues externally to the ovens, not inside them; since in the latter case too much heat is abstracted from the ovens, and

their temperature is not so high as is desirable for the proper working of the coking-process.

From a recent paper of Mr. H. Simon's * it appears that there are now at work three plants of Simon-Carvès ovens on the new system, comprising 50, 35, and 25 ovens respectively, all of them provided with recuperators. The ovens at Bear Park are a foot longer than those at Crook, and take a charge of 4½ tons each, which requires rather more than 48 hours to work off, owing to irregularities over night and on Sundays. It is claimed that these ovens are much more substantial than those on the Coppée system, with their extremely thin walls, which are liable to burn away at the intense heat prevailing, whilst it is impossible to inspect them; also that it is most difficult to split up the current of hot gases equally all over the small flues of the Coppée system, and that the gases, rushing through the six-feet length of these vertical flues, have not time to part with their heat, whilst in the Carvès oven the gas has to run more than 100 feet in one undivided current. Consequently the recuperators in the former system have much more work to do than in the latter. Lastly, it is urged that a continuous process of recuperation must yield more uniform results than one rising and falling with the change of regenerators. The coke from the new ovens fetches a higher price than any other coke for use in cupola furnaces; so far as blast-furnaces are concerned, there still seems to be some prejudice in England, which has been quite overcome in France, Germany, and Belgium.

The condensing-plant is of a very simple description, but as efficient as could be desired. An attempt to replace the rotary exhausters (p. 65) by Körting's injectors has failed.

From further notes, kindly supplied to the author directly by Mr. Henry Simon, it appears that the *yield of coke* is about 77 per cent. in Durham, 69 per cent. in Accrington, 62 per cent. in Staffordshire. The *yield of ammonia*, expressed as sulphate, is 1 per cent. to 1·25 per cent. with North-Country coal, and about 2 per cent. with Staffordshire coal. The *yield of tar* varies from 3 per cent. to 4 per cent., of about 1·1 specific gravity on the average, the quality being equal to any other high-temperature tar. The air is heated in the recuperator to some 430–480° C., and the temperature in the various flues is distributed somewhat

* Journal of the Iron and Steel Institute, No. 1 for 1885.

as follows:—In the top flue C′ (figs. 14 and 16) it is 1130–1180°; in the second flue (where more air is introduced) 1260–1278°; in the third flue 1100–1120°; in the lowest side-flue 1125–1130°; in the flues C below the oven-sole 1540–1565° C. Copper may be melted in the top flue, and iron will melt in the flue underneath the oven-sole. Only best Dinas bricks can be employed in some of the flues, as the best obtainable material will alone resist such intense heat. The distribution of the heat is very even throughout the sides of each oven, so that the available coking-space is utilized to the fullest extent. The coal is filled nearly to the top of the arch and levelled evenly, even close to the doors; whilst in other ovens, which do not distribute the heat so well, a portion of the space close to the door is lost for carbonizing. It is claimed that, on account of the extreme simplicity of construction, the expense of erecting these ovens is very moderate, and their maintenance is also very inexpensive.

The very great difference in the cost of the Otto ovens in Westphalia (p. 60) and the Simon-Carvès ovens at Crook (p. 66) is probably explainable in the following way, according to my opinion:—

The Crook ovens are not combined with a recuperator; they are very much smaller than the former (the charge being 4½ tons against 6½ tons each); the cost of firebricks in Westphalia is about twice as high as in Durham, and that of ironwork no doubt is also higher; the Westphalian condensing-plant is very much more extensive than that at Crook, all machinery being provided in duplicate, in case of accidents; there is, in addition to the Crook plant, a large gasholder, the Feldmann ammonia apparatus, and a substantial block of buildings to contain the whole condensing-plant and machinery. It is therefore not possible to institute a direct comparison between the cost of the two systems from the figures given here. That the Carvès ovens by themselves are not less, but rather more, expensive than the Otto ovens under *equal* circumstances, would appear from the cost of Hüssener's ovens (see below), which are decidedly less complicated than the Carvès-Simon ovens, according to the new (recuperator) system.

Another modification of Carvès ovens, equally provided with an air-heating apparatus, has been introduced into Germany by A. Hüssener (G. P. 16923 and 20196). *Hüssener's ovens*, of which 100 have been erected in Westphalia, are shown in figs. 18–20.

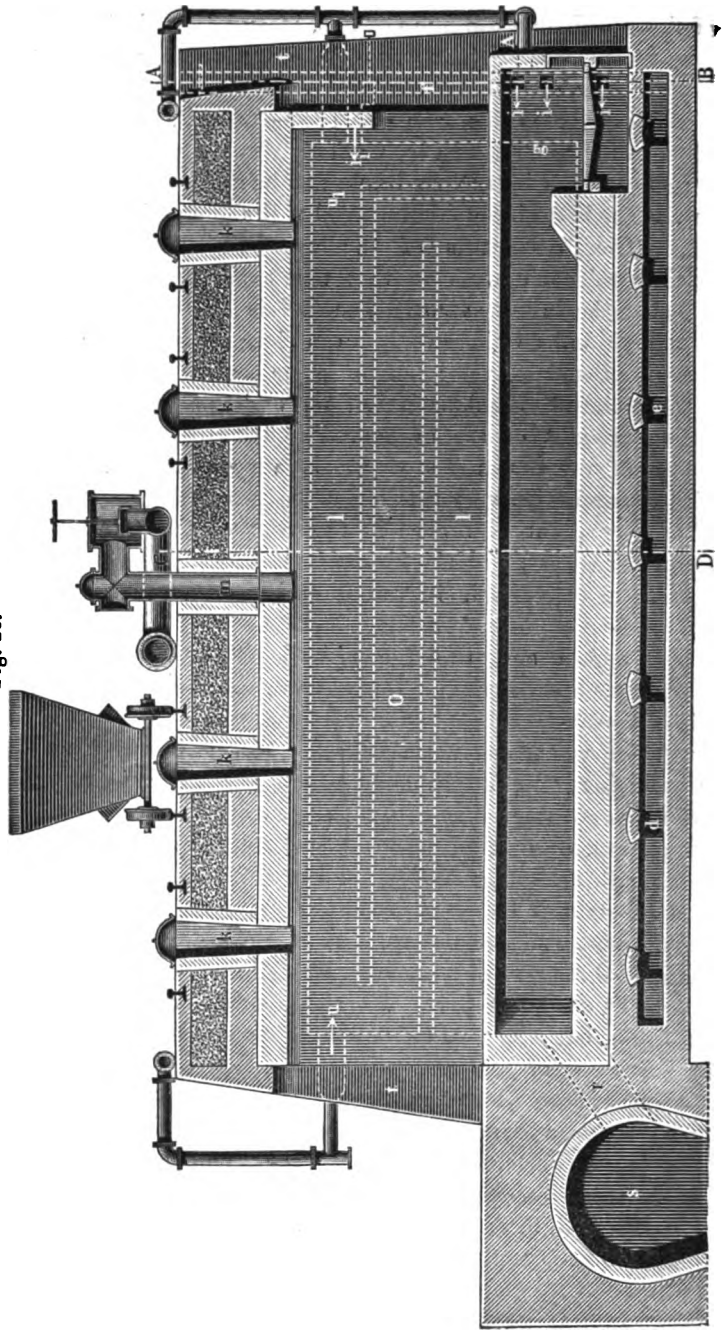

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Fig. 18.

Fig. 19.

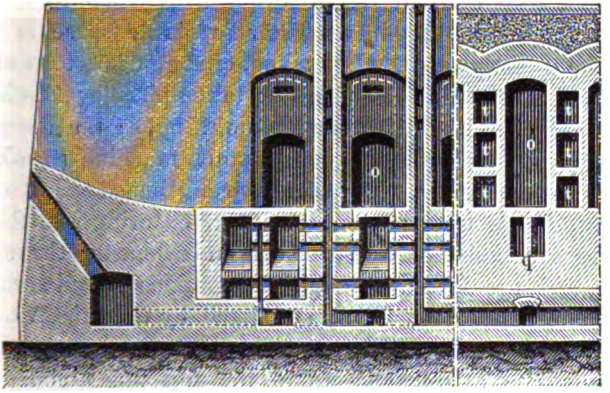
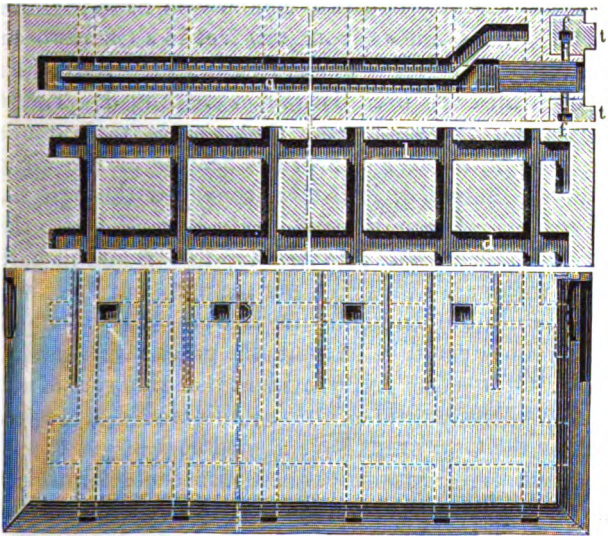


Fig. 20.



Their dimensions are: length 29 ft. 6⅜ in., width in the middle 1 ft. 10⅝ in., with a certain taper to facilitate the mechanical pushing out of the charge (as is usual in the case of all horizontal ovens, both those on the Coppée and on the Carvès system); height 5 ft. 10⅞ in. (the original Carvès ovens at Terrenoire are 19 ft. 8¼ in. × 2 ft. 5⅝ in. × 4 ft. 9 in.). Their available space is 88 per cent. of the total space, and they take a charge of 5½ tons of finely sifted, dry coking-coal. The charging takes place by 4 holes, *k k*; the ends are closed by doors turning on hinges; the discharging takes place by the ordinary pushing-out machine (ram). The end walls between each two ovens are strengthened by buttresses *t*, which at the same time prevent air from entering into the flues. The gases are aspirated by means of an exhauster through the outlet *m*, and are forced through the condensers and scrubbers; they then return to the ovens, and issue by the tube A over the fire-grate *g*, where they take fire. The fire-gases travel round the partition *q*, rise at one end up to the top flue *l*, and descend through the three horizontal flues *l l* and the snore-hole *r* into the main-flue *s*. The mouth of the gas-inlet pipe A is an annular double tube, like a Bunsen burner; whilst the inner tube conveys the air for combustion, the combustible gas issues through the annular space, and both enter at the same time into *g*. Owing to the distance which the products of combustion have to travel before they reach the main-flue *s* (about 100 feet in a Carvès oven), they were formerly cooled down too much, and the ovens did not get hot enough, whilst the oven bottoms were fluxed. To avoid this Hüssener (about the same time that Carvès took out his new patent, p. 67) introduced a previous heating of the air to about 300° C. in the flues *d e*; it is then conveyed through the small flue *f*, contained in the buttress *t*, partly through *i* into the grate-space *g*, partly through i_1 into the top flue *l*, and in both places gets mixed with gas. This does not seem to have met with complete success; but after adding further gas-inlets at *u* and u_1, the fire on the grate *g* could be left out, the gases sufficing for heating the retorts. [It seems pretty evident that this sort of firing the ovens is not so economical as Otto's; this would also appear from the fact that the Otto ovens have a good deal of gas to spare.]

The cost of erecting a set of 100 Hüssener ovens in Gelsenkirchen (Westphalia), according to a published balance-sheet, was:—

For utensils.....	Marks 2,689·33	
„ buildings	113,225·38	
„ machinery and iron-work	416,624·43	
„ railway	38,193·48	
„ well and water-pond	30,953·60	
	M. 601,686·22 =	per oven, M. 6016·86 or, say, £300.
„ coke ovens.....	326,475·51 =	3264·75 = £163.
„ land	105,655·15 =	1056·55 = £52.
	M. 1,033,816·88 =	M. 10,338·16

Or, say, £50,169; per oven about = £502.

The ovens are charged, at intervals of 60 hours, with 5½ tons of bituminous (proper coking-) coals, (say, 700 tons per annum, or two thirds of the output of the Otto ovens).

They are stated by Hüssener ('Stahl und Eisen,' 1883, p. 405) to yield:—

	From gas-coal.	From coking-coal.
Large coke	61·70	75·00
Small coke	3·50	0·80
Coke-breeze	9·18	1·20
Tar	2·72	2·77
Sulphate of ammonia.	0·924	1·10

The ammoniacal liquor has 5° Tw. and contains 1·65 per cent. NH_3. The tar is very thin; its specific gravity differs but little from that of the ammoniacal liquor. According to an analysis, made in November 1882, it yielded:—

58·83	per cent.	distillate	0·59	benzol 80–100° C.
39·51	„	pitch	0·49	„ 100–140° C.
1·66	„	loss	0·39	solvent naphtha.
			1·37	pure phenol.
			0·95	pure anthracene.

The yield of phenol and anthracene is much higher than from ordinary gas-tar.

Quality of the Tar produced in various Forms of Coke-ovens.

We have already mentioned this subject on p. 18 (Behrens), p. 47 (Jameson), and on p. 59 (in connection with the Otto ovens); but it has been most extensively treated by Watson Smith,

whose communications will be found in the Journal of the Society of Chemical Industry, 1883, pp. 403, 495; 1884, pp. 9, 64; and 1885, p. 451. We must refer for details to those papers, and here only give a short abstract of their contents.

The tar or tar-oil from *Jameson's coke-ovens* has a specific gravity of 0·960 to 0·994. It contains no benzene, but very little toluene and rather more xylene. The largest proportion consists of oils boiling between 250° and 350° C., evidently belonging to the marsh-gas series; they are of little value for burning, and of but secondary value as lubricants. From the higher boiling-oils (up to the point at which pitch remains in the retort) a small quantity of paraffin, melting at 58°, separates. By treating the crude oils with caustic soda a fair amount of phenols was extracted; but they contained no carbolic acid, by far the largest proportion distilling between 235° and 300°, and they appear to resemble the complicated phenols found in wood-tar creosote. Neither naphthalene nor anthracene is present. Altogether the Jameson tar evidently belongs to the class of tars obtained by the distillation of coal at lower temperatures, and cannot be classed with the ordinary gas-tar. Watson Smith considers them an excellent material for creosoting timber. The results of Watson Smith entirely coincide with those obtained in 1873 by Behrens with the tar from Pauwels' coke-ovens (p. 18).

H. E. Armstrong (Journ. Soc. Chem. Ind. 1885, p. 451) expresses the opinion that the Jameson tar or oil might be improved by passing it through red-hot retorts, and is thus "intrinsically" more valuable than the tar from closed coke-ovens. This idea, as well as his opinion that the construction of the beehive or the Jameson ovens more nearly approaches the ideal of a coke-oven than the closed ovens of Carvès and others, is directly opposed to my opinion, and probably to that of most competent observers. Mr. Watson Smith, who had already in 1883 conceived the plan of treating the Jameson oils as suggested by Armstrong, and who was on the point of patenting it but relinquished this plan, states as his reason for doing so, that the expense and losses of this process are ruinous unless these oils are to be had for almost nothing, and I entirely agree with that opinion.

A recent analysis of another sample of Jameson tar by Watson Smith ('Industries,' 1886, p. 162) has in every way confirmed the conclusions formerly arrived at.

The tar from the *Simon-Carvès ovens*, as produced from Pease's West coals, is black and thick, of specific gravity 1·106, and closely resembles the tar produced in the London gas-works, in containing very much naphthalene and anthracene, but less benzene, toluene, xylene, and carbolic acid than Lancashire tars. Paraffin is altogether absent. A fractional distillation of 2400 c. c. yielded:—

Below 120° ...	6·2	per cent. by vol. water.
„ „ ...	1·6	„ „ naphtha.
„ 210 ...	2·9	„ „ oil.
„ 220 ...	1·3	„ „ „
„ 230 ...	0·5	Nearly all solid naphthalene.
„ 300 ...	18·6	Naphthalene and anthracene, mixed with intermediate oils.
Above 300 ...	34·2	Nearly all solid crude anthracene; little red oil.
Residue ...	30·5	per cent. by weight half-coked pitch.

The pitch-coke was saturated with ammonia.

A determination of the real anthracene by Luck's method yielded 0·73 per cent., comparatively a very large amount, the freedom from "red oils" being much to the benefit of the alizarin makers. The benzene seems to be very rich in thiophene.

An analysis of the Simon-Carvès tar from Pease's West, by S. A. Sadler, yielded 4·5 per cent. by volume of light oils, 20·4 per cent. by volume of creosote oils, with much naphthalene, and 34·2 per cent. of thick anthracene oil. Further treatment of the distillates gave:—

	Per cent. on tar.
Water	10·00
Benzol 50/90 per cent.....	0·50
Solvent naphtha (90 per cent. at 160° C.).....	0·60
Heavy naphthas	0·40
Crude carbolic acid	0·05
Creosote oils.....	46·50
Anthracene	0 74
Pitch and loss	41·21
	100·00

From another set of Simon-Carvès ovens, erected at Bear Park, and working with a different description of coal at a somewhat higher temperature, the following results were obtained (Watson Smith, Journ. Iron and Steel Instit.) :—

	(*a.*)	(*b.*)	(*c.*)	
Ammonia water	...	...	7·44	per cent.
Light oils	5·12	5·12	6·28	„
Creosote oil	7·44	...	11·99	„
Naphthalene	...	...	10·17	„
Thick anthracene oil	34·03	...	...	
Crude anthracene	...	...	11·57	„
Naphtha	3·05	...	...	
Pitch	45·17	...	57·29	„

Further treatment gave :—

50/90 per cent. benzol	0·703	...	per cent. on tar.
Benzol boiling 80–100°	...	0·53	„ „
Toluol „ 100–120°	...	0·29	„ „
Solvent naphtha 90 per cent.	1·031	1·25	„ „
Burning naphtha 30 per cent.	0·434	0·20	„ „
Carbolic acid (crude)	0·305	...	„ „
Cresol (crude)	0·352	...	„ „
Naphthalene (crude)	...	1·00	„ „
Anthracene 28 per cent.	2·396	...	„ „

Specific gravity of tar=1·15. 1 ton of tar yielded 1·44 gallon of 50-per-cent. benzol and 48·2 lb. of 28-per-cent. anthracene.

The Bear-Park tar is seen to resemble normal retort-tar much more closely than the Pease's West tar; it contains much more benzol and carbolic acid than the latter (although less than the lowest average of carbolic acid from gas-retort tar, viz. 0·5 per cent.). It is rather less rich in naphthalene and anthracene, but still contains a great deal of those substances.

An analysis of tar from the Otto ovens has been quoted, p. 59.

The idea has been thrown out (mentioned in Mr. Weldon's presidential address, Journ. Soc. Chem. Ind. 1883, p. 8) that alkali-makers and other manufacturers, whose establishments are situated in coal-districts, instead of feeding their furnaces with coal in the usual manner, should become coke-producers—the coke-oven gas, along with the coke, to be their fuel, whilst the tar (or oil) and ammonia were to pay for the small coal or "duff" to be

employed. Thus they would get their fuel virtually for nothing Splendid as this conception is, a sober examination of the facts soon shows that it is impracticable, most certainly with the Jameson process which Weldon had in view. Whether it is more practicable, when so employed, to convert all the coal at once into "producer-gas," with recovery of the by-products, we shall see later on. I. Levinstein (*eod. loco*, p. 217) certainly believes that the suggestion mentioned by Weldon would be practicable for any manufacturer consuming at least 300 tons of coal per week, and subjecting the gas to the action of a fatty absorbent in order to recover the benzol; but we have seen above (p. 33 *et seq.*) that the absorbing processes are still on their trial. Levinstein holds that the coke and the gas will be practically equivalent in heating-power to the coal carbonized; but this evidently cannot be the case, since the tar is taken out and all the heat imparted to the gases in the coke-oven must be lost in cooling the gases for the recovery of the by-products. Scheurer-Kestner (Compt. Rend. vol. xcvii. p. 179) calculates the loss of calorific power in transforming coal into coke and gas at 19·3 per cent.

C. *Tar (and Ammonia) from Gas-producers.*

Since it had been proved that the process of coking coal can be performed to advantage in connection with a recovery of tar and ammonia, it was a very natural idea to extend this recovery to the gas from "gas-producers" or "generators." Attempts to solve this problem have been made in various quarters, but we shall here only mention the processes of Sutherland and Mond.

Sutherland (B. P. 3891, 1883) adds to the coal a substance capable of evolving hydrogen, and at the same time giving out an acid. He prefers for this purpose a solution of calcium chloride. Superheated steam is also employed, by combining two gas-producers with a continuous superheater and a steam-supply, the heated gas from one of the producers doing the superheating work; the hot steam, passing through the second producer, causes therein an action between the carbon of the fuel and the steam, whereby "water-gas" is produced. The gases are passed through suitable apparatus for separating the tar and ammoniacal products. The details of the producer and superheating apparatus cannot be given here.

An examination of the tar from Sutherland's gas-producers has been made by Watson Smith (Journ. Soc. Chem. Ind. 1884, pp. 9 & 64). Its specific gravity is 1·08; it is more like ordinary gas-retort tar than Jameson coke-oven or blast-furnace tar, but it has a different smell. By distillation there was obtained from it:—

Below 230° ..	5·44	per cent.	by vol.	oil of sp. gr.	0·956
From 230–300°	10·10	„	„	„	0·996
From 300° till oils solidified	14·48	„	„	„	0·990
Oils solidifying on cooling..	10·40	„	„	„	0·996
Coke.....	30·50	per cent.	by weight.		
Loss and water.	32·60	„	„		

On redistilling the first three fractions there was obtained:—

Below 160°	0·16	per cent.	by vol.	on tar of oil.
A. 160–210°.....	0·90	„	„	„
B. 210–220°.....	2·04	„	„	„
C. 220–230°	15·50	„	„	„
300° till oils began to solidify	6·96	„	„	„
Soft paraffin scale..	2·76	„	„	„

The oils A B C were light yellow, but darkened on standing. There was some phenol present, but no carbolic acid could be separated out. Naphthalene and anthracene were absent; of benzene but little, if any, is present. Of paraffin 6·7 per cent. on the tar could be separated.

The Sutherland-producer tar is thus seen to be entirely different from gas-tar, and is much similar to the Jameson-oven tar, but more impure than this. It is so thick that it can hardly be employed directly for creosoting without redistilling.

Several patents have been obtained by L. Mond for separating tar and ammonia from producer-gas (B. P. 3821 and 3923 of 1883, and 8973 of 1885), but as the principal stress is here evidently laid on the recovery of the ammonia, and the quality of the tar is not likely to be essentially different from that of the Sutherland-producer tar (a low temperature being expressly insisted upon), we shall treat of that process only in Chap. XII.

It should be noted that, apart from the patents actually taken out, attempts have been made in various quarters to recover by-

products from producer-gases, but none of them with any financial success. The examination of a producer-tar (not derived from Sutherland's producers, but from another source), according to a private communication made to the author, has shown that it contained a comparatively large quantity of anthracene, but unfortunately at the same time so much paraffin that it would be impossible on a manufacturing scale to oxidize the anthracene to anthraquinone; while, on the other hand, the paraffin obstinately retained some anthracene in spite of all purifying processes—the two substances thus mutually destroying their value.

D. *Tar (and Ammonia) from Blast-furnace Gases.*

The great majority of blast-furnaces are fed with coke, and it is evident that we cannot expect to recover either tar or ammonia from the waste gases of such furnaces. But it is otherwise with those furnaces that are fed with raw coal, in which the upper part of the furnace may be said to constitute a coking-chamber. Such an instance occurs in the West of Scotland, where there are vast beds of coal known as "splint coal" *. This coal is admirably adapted for direct use in blast-furnaces, since certain varieties of it agglomerate very little during coking and do not decrepitate. Scotch splint coals contain on the average 40 per cent. of volatile matter, of which 28 to 35 go to form tar, gas, &c., and they yield on the average 50 to 55 per cent. of fixed carbon. Were the average amount of nitrogen they contain (1·35 per cent.) all evolved as ammonia, this would correspond to 142½ lb. of pure sulphate per ton (6·36 per cent.); but in blast-furnace practice only from 17 to 20 per cent. of the nitrogen of the coal is converted into ammonia. As early as 1845 Bunsen and Playfair recommended the recovery of such ammonia from blast-furnace gases, and calculated that the Alfreton furnace would yield 9½ kilog. per ton. W. Jones makes the following calculation for the Scotch blast-furnaces:—Each ton of coal may be said to yield, on an average, 16 per cent. of its nitrogen as ammonia, that is equal to 22·8 lb. of ammonium sulphate, and from 120 to 220 lb. of tar, partly in the form of vapour at the temperature of the escaping gases, partly in the state of suspension.

* W. Jones, Proc. Iron and Steel Institute, 1885; Journ. Soc. Chem. Ind. 1885, p. 737, where analyses of such coal are given.

These substances, along with a very considerable amount of dust (which must be got rid of before tar and ammonia are condensed), are contained in a volume of gas corresponding to 125,000 cubic feet at 15°·5; but as the actual temperature varies from 204° to 343°, the gas will at, say, 260° C. occupy over 230,000 cubic feet, increased by 300 to 400 lb. of water per ton of coal in the form of vapour. This is thirteen times the volume of gas per ton of coal compared with that obtained in the manufacture of illuminating-gas in ordinary fireclay retorts.

From this enormous volume of gas, issuing out of the blast-furnace throat, the tar and ammonia are to be condensed. For this purpose it is best, according to experience, to maintain an outward pressure on the gas. A suction or inward pressure may not only lead to disastrous explosions, but it very much reduces the yield of ammonia, owing to the entrance of air and the consequent combustion of the ammonia. The tar in the gas is scrubbed out with great difficulty, owing to its peculiar physical condition and its state of suspension in such a large volume of gas. No amount of cooling and washing is so effective as some form of violent mechanical action, such as dashing with water or otherwise.

If the whole of the gases of the furnaces at present in blast in Scotland were to be treated for the recovery of ammonia, the turn-out of ammonium sulphate would be some 18,000 tons per annum, equal to 22 per cent. of the present production of Great Britain.

The different methods for recovering volatile products from blast-furnaces may be grouped as follows:—

(I.) Methods depending on the condensation or cooling of the gas.

(*a*) Alexander and McCosh process, as practised at the Gartsherrie iron-works.

(*b*) Dempster process (B. P. 11,250, 1884).

(*c*) Henderson process.

(II.) Methods depending upon the use of acids, without the cooling of the gas.

(*a*) Neilson's process, or Summerlee method (B. P. 440, 1882).

(*b*) Addie's process, or Langloan method (B. P. 4758, 1882).

(*c*) Chapman's process (B. P. 6406, 1884).

(*d*) Main and Galbraith's process (B. P. 10,448, 1884).

Most of these processes principally, or even exclusively, tend to the recovery of the ammonia only, and will therefore be mentioned in Chap. XII.; in this place we shall describe the principal process by which tar or oil can also be obtained from blast-furnaces.

The *Gartsherrie method* (Alexander and McCosh's patents, B. P. 4117, of 1879; 1433, of 1880; 3785, of 1881) is illustrated by figs. 21 and 22 (p. 88). The gases pass from the furnace by the main pipe G, through pipes *g*, the number of which is in proportion to the temperature and amount of the gases, into the coolers K, consisting of series of upright tubes, connected with each other alternately above and below, so that the gases take the course indicated by the arrows. Cooling takes place by reason of the large surface exposed by the pipes to the air. The pipe which connects the lower ends of these tubes also serves to collect condensed liquids, tar, and ammonia water; these are not permitted to rise to such a height as to obstruct the passage of the gas, but are drawn off by the overflow-pipe *u* to the tank T. The whole, as we see, is practically a copy of the ordinary air-condenser employed at gas-works. The gases pass through *z* into the washing-towers or scrubbers W, provided with perforated shelves of wood or metal, leaving alternately an open passage on one side or the other of the scrubber. A stream of water trickles from *w* down these shelves; the tar and ammonia, which have escaped condensation in K, are here condensed partly by the action of the water spread over a large surface, and partly by the continuous impact against the shelves, and pass down from W into T and S. The watery liquid which collects in S is pumped by P to the top of the towers, and used repeatedly, until sufficiently enriched with ammonia. The cooled and washed gases proceed by *x* to the second main G_1, to be utilized as required. If it be desired simply to eliminate flue-dust, the towers are unnecessary; but it is advisable in such a case to moisten the gases before they enter the coolers. A special apparatus for this purpose has been described by Belani*. I. Alexander has also constructed cooling and washing chambers of very great efficiency†, offering an extremely large area of water-cooled and air-cooled surface.

The *tar recovered from blast-furnaces* has been repeatedly exa-

* Dingler's Journal, vol. cliv. p. 257; Journ. Soc. Chem. Ind. 1885, p. 218.
† Ibidem.

Fig. 21.

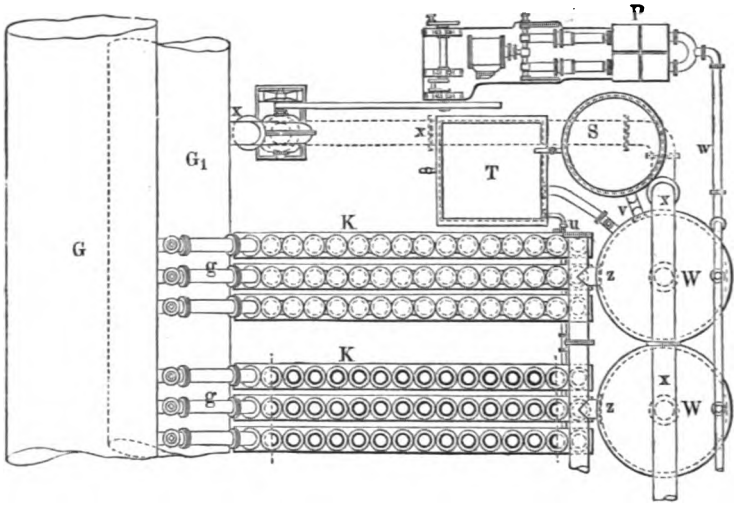
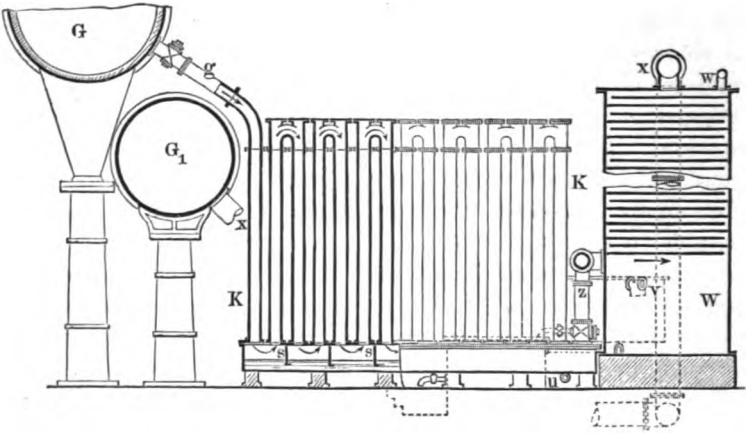


Fig. 22.



mined by Watson Smith (Journ. Soc. Chem. Ind. 1883, p. 495; Journ. Chem. Soc. 1886, vol. xlix. p. 17). Its specific gravity was found = 0·954. Distillation yielded:—

	Per cent. by volume.	Per cent. by weight.	Sp. gr.
Below 230° { water	30·60	32·3	1·007
Below 230° { oil	2·91	2·8	0·899
230° to 300°	6·97	7·1	0·971
300° until oils solidify...	13·02	13·5	0·994
Oils solidifying on cooling (soft paraffin scale) ...	16·75	17·3	0·987
Coke	...	21·5	
Loss	...	5·5	

The oils were quite transparent, the lower-boiling and lighter fractions possessing an amber-yellow colour, the higher-boiling ones having a colour approaching that of port wine. On standing a day or two they all considerably deepened in colour, especially the heavier fractions, which possessed a strong green fluorescence.

A further examination of the distillates proved that naphthalene is present in very small quantity; anthracene could not be detected, but small quantities of toluene, xylene, and pseudocumene were isolated. The xylene proved to consist principally of the meta-isomer (priv. comm. from Watson Smith). About 0·54 per cent. of hard paraffin was obtained from the tar, and a considerable amount of phenols, among them true carbolic acid. By successive treatment with caustic soda and sulphuric acid, the distillates answering to the carbolic-oil and creosote-oil of ordinary coal-tar yielded 23·1 per cent. by volume (on the tar) of phenols, and 11·09 per cent. by volume of basic substances.

This large proportion of phenols, far exceeding what can be obtained in a similar manner from ordinary gas-retort coal-tars, seems to some extent to confirm the theory of K. E. Schulze (Annalen, vol. ccxxvii. p. 143), according to which at least a considerable proportion of the aromatic coal-tar hydrocarbons is formed by the breaking-up, at higher temperatures, of first-formed phenols into the elements of water and hydrocarbons. Since blast-furnace tar, both on account of its being formed in the top part of the furnaces and also because of its chemical and physical properties, is evidently a low-temperature product as compared

with the tar obtained from gas-retorts and close coke-ovens (Carvès', Otto's, &c.), it might *à priori* be supposed that it was an intermediary mixture, and to contain, so to speak, the halfway phenol constituents in predominating quantity. On the contrary, it contains but a small quantity of the lowest phenol (carbolic acid), $C_6H_5 . OH$, and cresols, $C_6H_4(CH_3) . OH$, much less than gas-retort tar, which would seem to show that Schulze's theory can hardly extend to the formation of benzene itself. The decomposition of the higher-boiling phenols of blast-furnace tars by means of hot zinc-dust or hot iron-borings yielded a large quantity of xylenes, and proved the original presence of metaxylenol, $C_6H_3(CH_3)_2 . OH$, in accordance with Schulze's theory; the still higher-boiling fractions, treated in the same way, indicated the presence of pseudocumenol, $C_6H_2(CH_3)_3 . OH$, and of naphthols, $C_{10}H_7 . OH$. Of course other phenols and phenol-ethers might also be present.

In any case blast-furnace tar is altogether different from ordinary gas-retort tar, and cannot be employed for the same purposes. It would require to be redistilled, and would then yield creosoting oils of good quality and lubricating oils of indifferent quality.

E. *Preparation of Mixtures similar to Coal-tar by the Decomposition of certain Vapours at a High Temperature.*

The decomposition of compounds belonging essentially to the "fatty series" by passing their vapours through red-hot tubes, and the fact that aromatic compounds are formed in this way, has been principally studied by Berthelot (1867) and several other chemists. The preparation of illuminating-gas, which always contains considerable quantities of aromatic compounds, from oil and other fatty matters has been practised according to this method for a long time. But although the discovery of benzene itself, by Faraday, was made in the liquid condensing from compressed oil-gas, it is only quite recently that the preparation of substances similar to coal-tar—that is, containing considerable quantities of benzene, naphthalene, and anthracene—from the heaviest distillates and residues of the petroleum and paraffin-oil refineries, by passing them through red-hot tubes, has been attempted on a practical scale. Special experiments to ascertain how far this reaction might be applicable on a practical scale were called forth by a prize offered in 1877 by the Berlin Society for

the Promotion of Industry. It was required to be shown that converting the high-boiling oils of the browncoal-tar, by a technically applicable process, into the hydrocarbons forming the basis of the aniline-colour and alizarin industry is possible.

Liebermann and Burg* found that the above oils, when passed through red-hot tubes filled with porous material, are converted into a mixture of hydrocarbons very similar to coal-tar, containing about 4 per cent. benzene and toluene and 0·9 per cent. crude anthracene. Petroleum and vulcan oil yielded much gas and benzene, but hardly any anthracene. Coal-tar oils, boiling between 140° and 150° and between 150° and 210°, when treated in a similar way, suffered much less loss of weight. The quantitative results obtained by those chemists are, from their own showing, no guide as to those obtainable on the large scale, for which special experiments would be required. Similar to the above were the results of Salzmann and Wichelhaus†; and Atterberg‡ proved the same for wood-tar. The most extended paper on this subject has been published by Letny§. He examined a tarry condensate, produced in the manufacture of gas by passing heavy petroleum "tailings" through red-hot tubes filled with wood; after several passages through the retort he found it entirely similar to coal-tar, and especially proved it to contain benzene, toluene, xylene, naphthalene, anthracene, and phenanthrene, along with unchanged petroleum. After this he tried passing the petroleum-tailings on a small scale through a red-hot tube filled with charcoal. He obtained 33·3 per cent. of gas and 66·6 per cent. of tar, containing much amylene, benzene, toluene, xylene, and higher-boiling oils, but no solid hydrocarbons. The absence of the latter was ascribed by Letny to the comparatively small thickness of the layer of red-hot charcoal which the petroleum-vapours had to pass on the small scale. At a higher pressure more oils of low boiling-point were formed, but on the whole less tar and bad gas.

The raw material for Letny's experiments was the residue from refining the petroleum of Baku in South Russia (comp. Ch. IV.). Since it has been shown by Beilstein and Kurbatoff that this

* Ber. deutsch. chem. Ges. 1878, p. 723.
† Ibidem, pp. 802 and 1431. ‡ Ibidem, p. 1222.
§ Dingler's Journal, ccxxix. p. 353.

petroleum contains principally hydrogen addition-products of the benzene series, isomeric, but not identical, with the fatty compounds of the series C_nH_{2n}, it is easily explained how large quantities of benzenoid hydrocarbons could be obtained by the igneous decomposition of that substance.

In 1879 experiments made at my laboratory on a somewhat large scale by a chemist sent there by one of the largest Russian petroleum refiners (Ragosine), with an apparatus constructed by myself, fully confirmed the fact that large quantities of benzene, toluene, naphthalene, and anthracene could be obtained from petroleum residues in the above-described manner. In 1881, as reported by Rudnew*, in fact, the tar from the Kasan gas-works, where petroleum residues form the raw materials for gas-making, was distilled in the ordinary way; it yielded 10 to 12 per cent. of benzol, up to 5 per cent. of naphthalene, and some anthracene, but hardly any phenols.

In 1882, according to Liebermann†, the working-up of petroleum residues in the above-described manner was industrially carried out by the Brothers Nobel at Baku. The anthracene prepared by them tested 25 to 30 per cent., and at the Ludwigshafen works yielded quite good alizarin. The naphthalene was pure. The benzol, although boiling at 80° to 85°, was unsuitable for nitrobenzol, as it contained too many fatty hydrocarbons; but it can be easily purified by freezing at −14° (a process easily practicable in Russia during winter), even when containing 30 per cent. of impurities, and thus made to yield pure nitrobenzene, boiling at 205°. The naphtha residues are dropped into red-hot iron retorts filled with pumice; they yield, per 1000 kilog., 500 cubic metres (=17,650 cubic feet) of gas, employed for heating and lighting, along with 300 kilog. of tar, containing 0·6 per cent. of crude anthracene and 17 per cent. of crude benzol (boiling at 120°, and, indeed, containing only about 4 or 5 per cent. of benzene and toluene).

In the year 1882 there were produced at Baku 200,000 tons of naphtha residues, which are sold as fuel for steamboats &c. and for the manufacture of gas in Russia; but only a very small proportion of this was worked for benzol and anthracene. The outlay for plant is extremely large. Krämer found that, employing pipes 5 or 6 inches wide and 7 to 9 feet long, two set in one furnace, no

* Dingler's Journal, ccxxxix. p. 72.

† Dingler's Journal, vol. ccxlvi. p. 429; Journ. Soc. Chem. Ind. 1883, p. 128.

more than 2 cwt. of residues could be passed through in 24 hours. By his mode of purification he was able to prepare oils containing 91 or even 96 per cent. of nitrifiable benzol; whilst Liebermann's method yielded to him only oils containing 24 per cent. of nitrifiable benzol.

More recently, statements concerning the Russian trials of employing petroleum residues ("astatki") as sources of benzene, naphthalene, and anthracene have been made by B. Redwood (Journ. Soc. Chem. Ind. 1885, p. 79), from observations made during a visit to Baku in 1884. He mentions a "cupola regenerative furnace" patented by Nobel, and quotes the following details, obtained from that gentleman. The first treatment gives 30 to 40 per cent. of tar, containing 15 to 17 per cent. of 50-per-cent. benzol. By a second destructive distillation of heavy oils remaining in the tar after the separation of the benzol, 70 per cent. of tar is obtained, containing from 7 to 10 per cent. of 50-per-cent. benzol, 16 per cent. of naphthalene, 2 or 3 per cent. of dry "green grease" (or 30 per cent. anthracene), and 24 per cent. of pitch. There is also obtained in the process 75 to 100 cubic feet, per cubic foot of astatki, of gas having an illuminating-power five times greater than that of coal-gas. The regenerative furnace is first heated to 1000° C. (astatki being, of course, the heating-agent), and after having become cooled during the process of decomposing the astatki, it is again similarly heated, the gas remaining in the furnace and the coke deposited on the hearth being utilized as fuel. The furnace is stated to remain in working order without cleaning for twelve months. The process, in spite of being carried out on a somewhat large scale, had evidently not passed beyond the experimental stage, and has no doubt been stopped since Redwood's visit, owing to a fall in prices. Engler, who visited the same district in 1885, reports nothing of it.

Another trial of the same method has been made in the United States by a Swiss chemist, who had seen something of the experiments made in the Zurich laboratory (see above); but although a good deal of capital was sunk in the enterprise, the result was most unsatisfactory, either owing to that chemist's inexperience or to the adverse nature of American petroleum residues, which do not seem to have the same composition as the similar material obtained in the Caucasus.

General Observations on Coal-tar from various Sources.

All the above-mentioned varieties of coal-tar, to which we might add natural tars—as the Rangoon naphtha and, in a wider sense, even crude petroleum—are principally (although never exclusively) composed of hydrocarbons; but these belong to very different classes, and the members of these classes are present in various proportions. In some of them the "aromatic" hydrocarbons—that is, those belonging to the benzene series in its widest sense—are altogether predominant; and these "*benzenoid*" tars are those which yield the raw material for the manufacture of coal-tar colours—benzene, toluene, xylene, naphthalene, anthracene, and carbolic acid. In other tars, which we call the "*paraffinoid*" tars, we find, apart from phenols of higher orders, the members of the paraffin series and others closely related to it, as the olefines, all of them belonging to the "fatty" compounds. Some of these tars are stated to contain compounds which, although isomeric with paraffins or olefines, are yet in reality aromatic compounds, namely, hydrogen addition-products (compare next Chapter); but this does not seem to make any practical difference in the way in which such tars can be utilized (that is, merely for the manufacture of burning and lubricating oils and of solid paraffin), while they are useless for the manufacture of coal-tar colours.

As a rule, the members of both series are found to a certain extent in all kinds of tar; and this is a rule without exception if we include the phenols, which are all "aromatic" compounds, and which do not seem to be ever absent in any tar. Those tars are most valuable which contain most benzenoid hydrocarbons; even a rather small proportion of paraffinoid hydrocarbons greatly lessens their value for colour-making, and any considerable admixture of such may make them practically worthless for that purpose. Benzol, containing many "unnitrifiable" oils, is not accepted by any aniline manufacturer; and anthracene containing paraffin is dreaded by every alizarin maker. Hence the practical value of some of the tar-producing processes described above is very questionable, since they yield a mixture of benzenoid and paraffinoid compounds containing too much of the latter kind. It is of course not impossible that good and cheap manufacturing methods will be found for separating these two kinds of compounds; but until that is the case, those

processes have no chance of competing with gas-tar and with some descriptions of coke-oven tars.

It is, of course, an important question, What are the conditions under which the formation of benzenoid or that of paraffinoid compounds predominates? We have seen before (p. 17) that differences of temperature have a great deal to do with it; but this does not account for everything. Without doubt the physical condition and the chemical composition of the coal distilled are of great importance: older fossils yield more benzenoid hydrocarbons, younger ones more paraffins and phenols (p. 21). But even when treating one and the same material, ordinary gas-coal or coking-coal, great differences are observed according to the mode of applying the heat. We will illustrate this by the following quotation from a paper by Watson Smith ('Industries,' 1886, p. 139) :—

"In the cases in which the benzenoid tars (those useful for coal-tar colours) are yielded, the condition which must be observed is an intense heat applied to a relatively thin layer of the fuel. If this condition be not observed, consecutive distillation occurs, in which, in the interior of the mass of coal (a comparatively bad conductor of heat), or in that part of the oven or retort in which the heat is less intense, products of the paraffinoid class mainly are first distilled at the lower temperature there existing, pass outwards to the exterior, and escape in such abundance into the highly heated oven or retort space, and thence are so rapidly drawn-off to the condensing arrangements that a large proportion of the paraffinoid matters still predominate in the product condensed.

"In the other case, however, in which the layer of fuel is sufficiently thin, sufficiently exposed on all sides to the intense heat, as fast as the constituents of the coal rearrange themselves to form the products at all, they do so almost directly to form the high-temperature products and benzenoid constituents, and the consecutive is almost entirely merged in a more or less direct process.

"The truth of these observations is well illustrated in the forms, mode of heating, and general arrangement of the ordinary gas-retorts, and in the Simon-Carvès coke-ovens, and, in opposition to them, the Jameson's adapted beehive coke-ovens, where the coal lies in a dense mass spread out on the floor of the same, which is not heated below; nor are the sides heated, but the heat is applied to the upper surface of the carbonizing fuel. Also, in another

form of the adapted beehive coke-oven the coal lies in a dense mass on the floor, which is heated strongly by flues passing below the floor or bed; but neither sides nor top are heated, and if the top were heated there would be too great a space between it and the fuel. In both the latter cases, paraffinoid tars are produced."

To this we need only add, that the same conditions for producing benzenoid tars, as exist in the case of gas-retorts and Simon-Carvès coke-ovens, are offered by the Otto coke-ovens and other similar forms; while the conditions for the predominance of paraffinoid compounds are also offered, as a natural consequence of their mode of action, by gas-producers and blast-furnaces working with coal.

Determination of the Yield of Tar and Ammonia from Coal.

It is, of course, desirable to know beforehand what amount of tar and ammonia a new description of coal may be expected to yield. Such estimations would certainly be far more important if tar and ammonia ever became the principal products of the distillation of coal; but we have seen above that this state of affairs, which at one time seemed to be approaching, is now once more relegated to a distant future. Under present circumstances the quantity and quality of the gas and the coke obtained in distillation are decidedly the primary considerations.

Still, it does occur now and then that either coal-owners or coal-consumers wish to enlighten themselves as to the yield of by-products from some special description of coal. Hitherto the only reliable means of arriving at that result has been to distil some truckloads of coal in the same retorts or ovens which are used for the ordinary manufacture, taking care that the by-products are separately collected. This is not very easy, especially so far as the tar is concerned, since there is always a good deal remaining from previous operations in the hydraulic main &c.; but it can be done by special care, and we have already noticed (pp. 22 & 23) such experiments performed at Munich and Paris.

This test is, of course, not always possible to perform, and it is very desirable to arrive at the yield of by-products by a test on the laboratory scale. Instead, however, of describing any apparatus or process for this purpose, the author would point out the difficulties of such testings. At the very least there ought to be provided an experimental retort, imitating the conditions on the

large scale as closely as possible. In the author's laboratory there is a small cast-iron D-shaped retort, 18 inches long and 6 inches high (inside measurement), with a head, cover, and gas-delivery tube, just like those of ordinary gas-retorts, in which about 10 lb. of coal can be distilled. Even here the conditions are very different from those of a real gas-retort; and we must expect to get a very different quantity of tar, and of quite different quality, from that which the same coal will produce in a full-sized fireclay gas-retort or a coke-oven. In the case of ammonia, also, the small distillation is no guide as to the large one. It is of course utterly hopeless to expect anything like trustworthy results when chemists (as is the case) work with even smaller apparatus, such as glass combustion-tubing, porcelain tubes, or gun-barrels. S. Schmitz* believes he can get good results in testing for ammonia by passing the gases evolved in distilling 10 or 15 grams of coal in a combustion-tube over red-hot coke contained in the first half of the tube; but here it is uncertain how much of the ammonia is derived from the coal distilled, and how much from the action of the gases and vapours on the coke, which always contains nitrogen (Chap. XII.). The gases are absorbed in dilute sulphuric acid, the liquid evaporated to a small volume with the addition of oxide of mercury, and the ammonia driven off by caustic soda. This method will at best allow comparative results to be obtained for different descriptions of coal, but it cannot be expected that these results will coincide with manufacturing practice.

* 'Stahl und Eisen,' 1886, p. 396.

CHAPTER III.

THE PROPERTIES OF COAL-TAR AND ITS CONSTITUENTS.

Coal-tar is a black, more or less viscid fluid of peculiar smell, of specific gravity 1·1 to 1·2, usually between 1·12 and 1·15; London tar averages 1·2, and sometimes comes up to 1·215; country tars are lighter; cannel-coal tars still more so*. It has been asserted by some that tar is more valuable the lower its specific gravity. In any case this could only be said of pure coal-tar; but since the tar from cannel coal, shale, &c., which contains more toluene and paraffin than coal-tar, is much lighter than the latter, the above criterion is not in any way to be depended upon.

Coal-tar is an extremely complex mixture of chemical compounds, some of which have not even been isolated as yet. Thus very little is known of the indifferent oils, occurring in its distillation, between the phenols and naphthalene on the one side, and anthracene oil on the other; neither do we know all the compounds existing in crude anthracene, and still less those constituting the pitch. Whether some of the constituents of coal-tar were already present in the coal, and are therefore simply evolved by the ordinary process of distillation, must be left an open question. It can hardly be doubted that coal contains aromatic compounds; some contend that it is entirely made up of such, and contains no free carbon at all. But it is another question whether any of these compounds are volatile, without change, at the temperature existing in the gas-retorts.

Tar contains nitrogenous compounds chiefly of a basic nature,

* It is strange that authors like Bolley, Wurtz, Girard and Delaire, Vincent, and others have stated the specific gravity of coal-tar to be equal to or below that of water. Evidently there has been confusion with tar from browncoal or bog-head &c.; and a wrong quotation of this kind has travelled from one book to another without criticism.

owing to the nitrogen always found in the coal, and sulphur compounds, derived from the pyrites &c. never absent in coal.

E. J. Mills (Journ. Soc. Chem. Ind. 1885, p. 326) gives the following ultimate analyses of London and of average Scotch cannel gas-tar :—

	London.	Scotch cannel.
Carbon.....	77·53	85·33
Hydrogen.....	6·33	7·33
Nitrogen	1·03	0·85
Sulphur	0·61	0·43
Oxygen.....	14·50	6·06
	100·00	100·00

Since tar always contains a considerable quantity of ammoniacal liquor mechanically mixed with it, we must expect to find all the constituents of the latter in the tar; also all those of the gas probably occur in the tar, being absorbed by it.

The following is an enumeration of the compounds hitherto found in coal-tar or reasonably presumed to exist in it; they will afterwards be described in detail.

	Formula.	Melting-point.	Boiling-point.
A. Hydrocarbons.		° C.	° C.
I. *Methane Series*, C_nH_{2n+2}.			
Methane	CH_4		
Ethane	C_2H_6		
Propane	C_3H_8	.....	−20
Butane (normal)	C_4H_{10}	.....	+ 1
Pentane (normal)	C_5H_{12}	liquid	37–39
Isopentane	C_5H_{12}	,,	30
Hexane (normal)	C_6H_{14}	,,	69–71
Heptane (normal)	C_7H_{16}	,,	98
Ethylisoamyl	C_7H_{16}	,,	90·3
Octane, I.	C_8H_{18}	,,	119–120
,, II.	C_8H_{18}	,,	124
Nonane, I.	C_9H_{20}	,,	130
,, II.	C_9H_{20}	,,	150·8
Decane, I.	$C_{10}H_{22}$	,,	158–161
,, II.	$C_{10}H_{22}$	,,	170–171
Undecane	$C_{11}H_{24}$	,,	180–182
Duodecane	$C_{12}H_{26}$	,,	200–202
Tredecane	$C_{13}H_{28}$	,,	218–220
Quatuordecane	$C_{14}H_{30}$	,,	236–240
Quindecane	$C_{15}H_{32}$	,,	258–262
Sedecane	$C_{16}H_{34}$	,,	280

	Formula.	Melting-point.	Boiling-point.
		° C.	° C.
A. Hydrocarbons (*continued*).			
I. *Methane Series* (continued)			
Paraffins	$C_{17}H_{36}$ to $C_{27}H_{56}$	40–60	
II. *Ethylene Series*, C_nH_{2n}.			
Ethylene	C_2H_4	.....	−110
Propylene	C_3H_6	.....	,,
Butylene (normal)	C_4H_8	.....	− 5
Pseudobutylene	C_4H_8	.....	+ 1
Isobutylene	C_4H_8	.....	− 8
Amylene	C_5H_{10}	liquid	+ 39
Hexylene	C_6H_{12}	,,	68–70
Heptylene	C_7H_{14}	,,	96–99
III. *Addition-products of the Benzene Series*, C_nH_{2n}.			
Hexahydrobenzene	C_6H_{12}	liquid	69
Hexahydrotoluene	C_7H_{14}	,,	97
Hexahydroisoxylene	C_8H_{16}	,,	118
Naphthenes (?).			
IV. *Acetylene Series*, C_nH_{2n-2}.			
Acetylene	C_2H_2		
Allylene	C_3H_4		
Crotonylene	C_4H_6	liquid	18
Valylene (?)	C_5H_8		
Hexoylene	C_6H_{10}	liquid	80
Higher members	$C_{12}H_{20}$	,,	210
,, ,,	$C_{14}H_{24}$	,,	240
,, ,,	$C_{16}H_{28}$	,,	280
V. *Series* C_nH_{2n-4}.			
Nonone	C_9H_{14}	liquid	174
VI. *Benzene Series*, C_nH_{2n-6}.			
Benzene	C_6H_6	4·5–7	80·4
Toluene	C_7H_8	liquid	111
Xylene	C_8H_{10}	,,	
Orthoxylene	.....	,,	141–142
Metaxylene	.....	,,	139
Paraxylene	.....	15	137·5–138
Pseudocumene	C_9H_{12}	liquid	169·5
Mesitylene	C_9H_{12}	,,	163
Hemellithol	C_9H_{12}	,,	175
Durene	$C_{10}H_{14}$	80–81	196
VII. *Styrolene* (?)	C_8H_8	liquid	145
Hydride of styrolene (?)	C_8H_{10}	,,	
VIII. *Naphthalene*	$C_{10}H_8$	79	218
Naphthalene dihydride	$C_{10}H_{10}$	liquid	200–210
,, tetrahydride	$C_{10}H_{12}$	,,	190
a Methylnaphthalene	$C_{11}H_{10}$	,,	240–243
β Methylnaphthalene	$C_{11}H_{10}$	32·5	241–242
Dimethylnaphthalene	$C_{12}H_{12}$	liquid	262–264

	Formula.	Melting-point.	Boiling-point.
A. Hydrocarbons (*continued*).		° C.	° C.
IX. *Acenaphthene*	$C_{12}H_{10}$	95	277·5
Acenaphthene hydride	$C_{12}H_{12}$	.....	260
Diphenyl	$C_{12}H_{10}$	70·5	254
Fluorene	$C_{13}H_{10}$	113	295
Anthracene	$C_{14}H_{10}$	213	360
Anthracene dihydride	$C_{14}H_{12}$	106	305
„ hexahydride	$C_{14}H_{16}$	63	290
Methylanthracene	$C_{15}H_{12}$	208–210	above 360
Dimethylanthracene (?)	$C_{16}H_{14}$	224–225	
Phenanthrene	$C_{14}H_{10}$	99–100	340
Pseudophenanthrene (?)	$C_{16}H_{12}$	115	above 360
Synanthrene (?)	$C_{14}H_{10}$	189–195	
Fluoranthene	$C_{15}H_{10}$	109	above 360
Pyrene	$C_{16}H_{10}$	148	above 360
Chrysene	$C_{18}H_{12}$	250	436
Chrysogen	.....	280–290	
Retene	$C_{18}H_{18}$	98–99	350
Succisterene?	.....	160–162	above 300
Picene	$C_{22}H_{14}$	345	518–520
Benzerythrene	$C_{24}H_{18}$	307–308	
Bitumen.			
B. Oxygenized Compounds.			
Water	H_2O	0	100
Methylic alcohol (?)	CH_4O	liquid	63
Ethylic alcohol (?)	C_2H_6O	„	78·5
Acetone	C_3H_6O	„	56
Acids and Phenols.			
Acetic acid	$C_2H_4O_2$	16	119
Benzoic acid	$C_7H_6O_2$	121	249
Phenol (carbolic acid)	C_6H_6O	42	184
Orthocresol	C_7H_8O	32	188
Paracresol	„	36	199
Metacresol	„	3–4	201
Xylenols: Ortho 1, 2, 4	$C_8H_{10}O$	62	225
Meta 1, 2, 3	„	73	216
Meta 1, 3, 4	„	26	211·5
Para 1, 3, 4	„	74·5	211–213
α Naphthol	$C_{10}H_8O$	94–96	278–280
β Naphthol	„	122	294
Phenols of the Anthracene series (?)		?	
α Pyrocresol	$C_{15}H_{14}O$	195	350
β Pyrocresol	„	128	
γ Pyrocresol	„	105	
Rosolic acid (?)	$C_{19}H_{14}O_3$		
Brunolic acid (?).			
C. Sulphuretted Compounds.			
Hydrogen sulphide	H_2S		
Ammonium sulphide	$(NH_4)_2S$		
„ sulphocyanide	$(NH_4)NCS$		

	Formula.	Melting-point.	Boiling-point.
C. Sulphuretted Compounds (*continued*).		° C.	° C.
Sulphur dioxide	SO_2		
Carbon bisulphide	CS_2	liquid	47
„ oxysulphide	COS		
Mercaptanes			
Alliol (?)			
Thiophen	C_4H_4S	liquid	84
Thiotolen	C_5H_6S	„	113
Thioxen	C_6H_8S	„	137
D. Chlorinated Compounds.			
Ammonium chloride	NH_4Cl		
E. Nitrogenized Compounds.			
I. *Basic.*			
Ammonia	NH_3		
(Ammonium compounds mentioned under C, D, & E II.)			
Methylamine, ethylamine, &c.	.....	liquid	
Cespitine (?)	$C_5H_{13}N$	„	95
Aniline	C_6H_7N	−8	182
Homologues of aniline (?).			
Pyridine	C_5H_5N	liquid	116·7
a Picoline	C_6H_7N	„	135
γ „	„	„	(?)
aa Lutidine	C_7H_9N	„	142
aγ „	„	„	157
$a\beta_1$ „	„	„	(?)
γ. Ethylpyridine	„	„	154
Collidine	$C_8H_{11}N$	„	179
Parvoline	$C_9H_{13}N$	„	188
Coridine	$C_{10}H_{15}N$	„	211
Rubidine	$C_{11}H_{17}N$	„	230
Viridine	$C_{12}H_{19}N$	„	251
Leucoline (Chinoline)	C_9H_7N	„	239–240
Isoquinoline	C_9H_7N	18–23	236–237
Chinaldin	$C_{10}H_9N$	liquid	243
Iridoline	$C_{10}H_9N$	„	252–257
Cryptidine	$C_{11}H_{11}N$	„	274
Tetracoline-Octacoline?			
Acridine	$C_{13}H_9N$	111	above 360
II. *Not Basic.*			
Pyrrol	C_4H_5N	liquid	133
Ammonium cyanide	$CN.NH_4$		
Methylic cyanide	$CH_3.CN$	„	77
Methylic isocyanide	C_2H_3N	„	59·6
Carbazol	$C_{12}H_9N$	238	355
Phenylnaphthyl-carbazol	$C_{16}H_{11}N$	330	above 440
F. Free Carbon	C_x		

Hydrocarbons of the Methane Series, C_nH_{2n+2}.

These hydrocarbons are sometimes called hydrides of monad radicals—also paraffins, because a mixture of the higher solid members of the series, as obtained in the distillation of shale &c., had obtained that name from its great resistance to chemical reactions (*parum affinis*). This mixture, however, contains also non-saturated hydrocarbons (olefines).

The compounds of this series are principally formed in the destructive distillation of wood, peat, shale, browncoal, bog-head, cannel coal, &c., and from coal also when distilled at a comparatively low temperature. Most descriptions of natural petroleum consist of a mixture of all the members of this series. In coal-tar they play a subordinate part; but if, in gas-making, coal has been partly replaced by browncoal, shale, cannel coal, &c., the tar is much richer in fatty hydrocarbons and may easily contain so much of them that the extraction of the aromatic hydrocarbons does not pay—especially as the fatty hydrocarbons are most objectionable impurities in commercial benzol, which, if they occur to any great extent, may make it unfit for the manufacture of nitrobenzol.

The compounds of this class are distinguished from the non-saturated hydrocarbons (the ethylene and acetylene series) by not being absorbed by sulphuric acid or bromine; this behaviour can be utilized for separating the two classes. From benzene and its homologues they are distinguished through being hardly at all acted upon by nitric acid in the cold, and not forming nitro-compounds.

The lowest members, up to butane, are at the ordinary temperature gaseous, but may occur in tar in a state of solution, all the more readily as they are easily soluble in ether and alcohol, and thus probably also in benzene &c. The members from pentane upwards are liquid; up to decane they have been observed in tar. The highest members, beginning from $C_{18}H_{38}$, are solid, and form paraffin proper: whether this occurs in tar obtained exclusively from ordinary coal is doubtful.

Methane, CH_4.

Synonyms—methylic hydride, marsh-gas, fire-damp, light carburetted hydrogen. A colourless gas, devoid of smell or taste. Sp. gr. 0·5566 (air=1). At 0° C. 100 vols. of water absorb

5·45 vols.; alcohol nearly half its volume. It burns with a pale yellow flame. Passed through red-hot tubes it yields acetylene, benzene, naphthalene. Mixed with air it gives very explosive mixtures.

Ethane, C_2H_6.

Syn. dimethyl, ethylic hydride. A gas without colour or smell; sp. gr. 1·075; condenses at 4° to a liquid under a pressure of 46 atmospheres. Water dissolves at 0° 9·45 per cent. by volume, alcohol 1½ times its volume. Burns with a bluish, non-luminous flame.

Propane, C_3H_8.

Syn. propylic hydride. A gas, condensing to a liquid below −20° C; alcohol dissolves six times its volume.

Butane, C_4H_{10}.

Syn. diethyl, butylic hydride. Two isomers are possible and known; only normal butane, however, $CH_3—CH_2—CH_2—CH_3$, has been found in mineral oils. Sp. gr. 2·01 (air=1). Authorities differ widely as to its boiling-point. Frankland puts it at −23°; Butlerow at +1°, and, under pressure of 2¼ atmospheres, at +18°. In water it is next to insoluble. Alcohol at 14° C. and 745 millim. pressure dissolves 18·13 vols. It burns with a strongly luminous flame.

Pentane, C_5H_{12}.

Syn. amylic hydride. Of the three isomers the normal and isopentane, $CH_3—CH_2—CH(CH_3)_2$, have been found in cannel and bog-head tar. Schorlemmer found in coal-tar only normal pentane.

Normal pentane boils at from 37° to 39° C., sp. gr. at 18°=0·6263 (water=1). Isopentane boils at 30°, sp. gr. at 18°=0·628. Both are colourless, very mobile liquids, something similar to chloroform, miscible with ether and alcohol in every proportion, solvents for fats; they burn with a brilliant white flame.

Hexane, C_6H_{14}.

Syn. caproylic hydride. Five isomers; the normal one occurs in petroleum, bog-head, and cannel tar; it is the principal constituent of the most volatile petroleum-ether (gasoline). Boils at 66–71°;

sp. gr. at 17° = 0·663. Colourless, mobile liquid, of faintly ethereal smell, insoluble in water, miscible with ether, alcohol, acetone, &c. (this solubility holds good for all the higher members as well). Burns with a bright, luminous flame.

Warren found another hexane in petroleum, boiling at 61°·3, which Schorlemmer could not discover in the same.

Heptane, C_7H_{16}.

Syn. œnanthylic hydride. Nine isomers possible. The different tars contain the normal one, boiling at 98°, sp. gr. at 0° = 0·7006, at 15° = 0·6886; also ethylisoamyl, boiling at 90°·3, sp. gr. at 0° = 0·6969. Mobile liquids, of faint, pleasant smell; burn with a somewhat smoking flame.

Octane, C_8H_{18}.

Syn. caprylic hydride, dibutyl, valyl. Of the eighteen possible isomers one boiling at 119° or 120° (sp. gr. at 17° = 0·719), and another, probably the normal one, boiling at 124° (sp. gr. at 0° = 0·7188), have been found in petroleum, boghead-, and coal-tar. They are limpid liquids with an ethereal smell and somewhat burning taste. The ordinary petroleum-spirit (benzoline) of commerce contains principally heptane and octane.

Nonane, C_9H_{20}.

That found in petroleum boils according to Wurtz at 130–132° (sp. gr. at 6° = 0·7242, smell like oranges); according to Beilstein at 150°·8. Which is right? Refined petroleum (kerosene) contains from C_9H_{20} up to $C_{16}H_{34}$, along with hydrocarbons of the formula C_nH_{2n}.

Decane, $C_{10}H_{22}$.

Syn. diamyl. Found in all tars, probably the isomer diisoamyl. Boils at 158–159°; at −30° it gets viscid; sp. gr. at 18° = 0·736. Beilstein states that the boiling-point is 161°, the sp. gr. at 16° = 0·757. O. Jacobsen * has found a decane, boiling at 170°–171°, in the fractions of light coal-tar oil which pass over between 163° and 168°, along with pseudocumene and mesitylene.

* Ann. Chem. clxxxiv. p. 179.

Undecane, $C_{11}H_{24}$.

Found in American petroleum. Boils at 180–182°; sp. gr. at 16°=0·765.

Duodecane, $C_{12}H_{26}$.

Syn. dicaproyl, dihexyl, laurylic hydride. Found in bog-head tar and petroleum. An oily colourless liquid, with a pleasant, turpentine-like smell, boils at 200–202°, sp. gr. at 18°=0·7568; burns with a luminous flame, without much smoke.

Higher members.

$C_{13}H_{28}$,	boiling-point	218–220°,	sp. gr.	0·778
$C_{14}H_{30}$	,,	236–240°	,,	0·796
$C_{15}H_{32}$	,,	258–262°	,,	0·809
$C_{16}H_{34}$	,,	about 280°		

Solid Paraffin

contains bodies of the formula $C_{17}H_{36}$ up to $C_{27}H_{56}$; also usually about 1 per cent. of oxygen. The paraffin found in the highest-boiling portions of real coal-tar is, according to Perkin, unlike ordinary paraffin; it fuses at a higher temperature, and is but slightly soluble in petroleum or naphtha. The proper paraffins occur principally in tar from Scotch and Lancashire cannel coal.

HYDROCARBONS OF THE ETHYLENE SERIES, C_nH_{2n} (OLEFINES).

The lowest members of this series are gaseous at the ordinary temperature, but occur constantly in illuminating-gas, and probably dissolved in tar. The higher ones are liquid; the highest, solid. It is characteristic of all to unite directly with chlorine, bromine, or iodine, forming oily liquids; with bromine especially the reaction is very violent. This is ascribed to the circumstance that they are non-saturated compounds ("dyad radicals"), in which carbon occurs doubly tied, so that, when one of these ties is broken, two monovalent atoms can attach themselves directly; *e. g.*

$$\underset{\text{Ethylene}}{H_2C{=}CH_2} + \underset{+\text{bromine}}{Br_2} = \underset{=\text{ethylene dibromide.}}{BrH_2C{-}CH_2Br}.$$

They also unite readily with the halogen hydrides HCl, HBr, and especially HI; also with hypochlorous acid, forming chlorhydrines,

e. g. $CH_2(OH)—CH_2Cl$. Concentrated sulphuric acid absorbs them, the lower members only at higher temperatures, also by direct attachment and formation of sulphonic acids; *e. g.*

$$H_2C=CH_2 + HO—SO_2—OH = HO—SO_2—OC_2H_5.$$
Sulphovinic acid.

From this it follows that these compounds can be removed from the tar-oils by bromine or by concentrated sulphuric acid. In ordinary coal-tar they play but an insignificant part; but they occur copiously in cannel-coal and bog-head tar.

Ethylene, C_2H_4.

Syn. elayl. Liquefies at 0° only under a pressure of 42½ atmospheres, at −110° under the ordinary pressure. Sp. gr. 0·9784. Water at 0° dissolves 0·25 vol.; at 15°, 0·16 vol. Much more dissolves in alcohol, ether, oil of turpentine, petroleum (about 2½ vols.), hence probably also in tar-oils. Concentrated sulphuric acid absorbs it on prolonged agitation, better at 160–175° C., fuming oil of vitriol much more quickly, with formation of ethionic acid. Armstrong and Miller* have found it in the "hydrocarbon" condensed from Pintsch gas, as well as propylene, normal amylene, normal hexylene, and normal heptylene.

Propylene, C_3H_6.

Syn. tritylene. Not yet liquid at −140°, possessing an alliaceous smell. 100 vols. of water dissolve at 0° 44 vols., at 15° 23 vols.; absolute alcohol 12–15 vols., glacial acetic acid 5 vols. Its chemical behaviour is like that of ethylene.

Butylene, C_4H_8.

Syn. tetrylene, ditetryl. Three isomers are possible and known. First condensed by Faraday from the lighting-gas obtained from fatty oils, by strong pressure. Normal butylene,

$$CH_3—CH_2—CH=CH_2,$$

boils at −5°; pseudobutylene,

$$CH_3—CH=CH—CH_3,$$

* Journ. Chem. Soc. xlix. p. 74.

at $+1°$; isobutylene,

$$(CH_3)_2C{=}CH_2,$$

at $-7°$ or $-8°$.

Amylene, C_5H_{10}.

Syn. pentylene, valerene. Of the five possible isomers, only that is well known which is obtained from amylic alcohol by water-abstracting reagents, especially zinc chloride. Whether this is identical with the amylene found in coal-tar * and much more abundantly in bog-head tar, petroleum, &c., or not, is not quite certain; but this is usually assumed to be the case. At all events several amylenes occur in tar, probably also polymers.

Ordinary amylene is a limpid, mobile liquid, of cooling, astringent, and somewhat pungent taste, and smelling somewhat like rotten cabbages. Its boiling-point is variously stated at from 33° to 42° (that obtained from amylic alcohol boils at 39°). Sp. gr. at $10°=0{\cdot}6549$. It is but sparingly soluble in water, but indefinitely miscible with alcohol. Like its congeners it unites directly with Cl, Br, HCl, HBr, HI, also with NO_2 and HOCl. Oxidizing substances (potassium permanganate, chromic acid, &c.) convert it into fatty acids, carbon dioxide, ketones, &c. With sulphuric acid, Berthelot says†, it yields an acid isomer to sulphamylic acid, which Erlenmeyer‡ could not find. However this may be, all the isomers dissolve in sulphuric acid at ordinary temperatures, some of them even when it is not fully concentrated.

Amylene was used for some time as an anæsthetic, in lieu of chloroform.

Hexylene, C_6H_{12}.

Syn. caproylene. Of the many isomers, tar seems to contain essentially the normal, the only one pretty well known; but other isomers are probably present as well. Normal hexylene is a colourless, mobile liquid, smelling like amylene, boiling at 68–70°; sp. gr. at $0°=0{\cdot}6996$; insoluble in water, readily soluble in ether and alcohol; chemically quite analogous to amylene. Sulphuric acid, diluted with $\frac{1}{3}$ vol. water, dissolves in the cold its volume of hexylene, from which mixture secondary hexylic alcohol soon separates.

* Helbing, Ann. der Chem. clxxii. p. 281. Watson Smith (priv. comm.) has also found amylene in the first runnings of London tar, along with carbon bisulphide.

† Compt. Rend. lvi. p. 1242.

‡ Zeitschr. f. Chemie, 1865, p. 302.

Concentrated sulphuric acid colours it reddish brown, gives off SO_2, and turns it into a thick oil.

Heptylene, C_7H_{14}.

Syn. œnanthylene. Like the above, found in bog-head tar. A limpid, mobile liquid with an alliaceous smell. Boils at 94° (Pelouze and Cahours), 96° (Schorlemmer), 99° (C. G. Williams). Sp. gr. at 18°=0·718 (C. G. Williams), at 17°·5=0·7388 (Schorlemmer). Its chemical behaviour is like that of the two foregoing compounds.

AROMATIC ADDITION-PRODUCTS, C_nH_{2n}.

According to Beilstein and Kurbatow*, the hydrocarbons of Caucasian petroleum having the formula C_nH_{2n} are not identical with the compounds of the preceding series; such occur also in American petroleum along with heptane &c. They were found identical with the hydrogen-addition products of aromatic hydrocarbons discovered by Wreden†, viz.:—

		Sp. gr. at 0°.	Boils at
Hexahydrobenzene	C_6H_{12}	0·76	69° C.
Hexahydrotoluene	C_7H_{14}	0·772	97
Hexahydroisoxylene	C_8H_{16}	0·777	118

Schützenberger and Ionine‡, who confirm the above, propose the name *paraffenes* for these compounds, inactive towards bromine, sulphuric acid, and nitric acid. Armstrong and Miller§ have found these saturated hydrocarbons of the formula C_nH_{2n}, which they call "pseudolefines," in the "hydrocarbon" condensing from Pintsch gas.

Markownikoff||, without denying the existence of hexahydrobenzene &c., declares that most of what has been taken for these compounds belongs to a new class of compounds which he calls "naphthenes," and of which very little is known up to the present.

* Ber. deutsche chem. Ges. 1880, pp. 1818, 2028.
† Liebig's Annalen, clxxxvii. p. 166.
‡ Compt. Rend. xci. p. 828.
§ Journ. Chem. Soc. xlix. p. 90.
|| Ann. Chem. Pharm. ccxxxiv. p. 89.

Hydrocarbons of the Acetylene Series, C_nH_{2n-2}.

Acetylene itself, C_2H_2, is a gas, and can only be dissolved in very small quantity in tar. Schorlemmer* has found in the light oil from cannel coal, after treatment with sulphuric acid, polymers of the acetylene series having the general formula $(C_nH_{2n-2})_2$, viz.:—

$C_{12}H_{20}$, boiling at 210° C.
$C_{14}H_{24}$ „ 240
$C_{16}H_{28}$ „ 280

They are colourless oily liquids, lighter than water, smelling like carrots or parsnips. They unite directly with bromine, with a violent reaction; in concentrated nitric acid they dissolve; and on diluting the solution with water, oily nitro-compounds separate. Since the original oils boiled below 120°, they cannot have contained these bodies, but those of the acetylene series, C_nH_{2n-2}, itself. In coal-tar they probably play even a less important part than in cannel-tar. But to acetylene itself a very important function in the formation of aromatic hydrocarbons is ascribed (see below).

Allylene, C_3H_4.

Normal allylene, $CH_3-C\equiv CH$, discovered in 1861 by Sawitsch and by Markownikoff. Colourless gas, smelling like acetylene, soluble in water and especially in alcohol.

Isoallylene, $CH_2=C=CH_2$, discovered in 1872 by Aarland.

The allylenes have not yet been proved to exist in coal-tar; but it is most probable that they occur there and play an important function like that of acetylene.

Crotonylene, C_4H_6.

Discovered in 1863 by Caventou; since then prepared synthetically and found in coal-tar† and in Pintsch tar‡. Possibly the latter is isomeric with the crotonylene from coal-tar, and is not a true acetylene. A colourless liquid, boiling at 18°. Probably ethyl-acetylene, $C_2H_5 . C\equiv CH$, or else dimethylene-ethane, $CH_2=CH-CH=CH_2$, or else dimethylacetylene,

$$CH_3 . C\equiv C . CH_3.$$

* Chem. News, xiii. p. 253.

† Caventou, Bull. Soc. Chim. [2] xix. p. 245; Helbing, Ann. der Chemie, clxxii. p. 281.

‡ Armstrong and Miller, Journ. Chem. Soc. xlix. p. 80.

Hexoylene, C_6H_{10}.

Syn. diallyl. A colourless liquid, with a penetrating alliaceous smell, boiling at 76–80°; sp. gr. at 13° = 0·71.

Hydrocarbons of the Series C_nH_{2n-4}.

One such, *nonone*, C_9H_{14}, the next lower homologue of oil of turpentine, has been found by Tawildarow* in tar, viz. in the portion distilling after cumene, between 175° and 190°. On fractionating, most came over at 174°. This body does not appear to have been obtained in a pure state; and its existence cannot be considered completely established.

Roscoe†, in "first runnings" from coal-tar, discovered a compound spontaneously formed by polymerization of the fraction boiling at 30°, and exhibiting the composition $C_{10}H_{12}$, melting at 32°·9. He considers it possible it may have been formed from *valylene*, C_5H_6, but a search for that body proved unsuccessful.

Hydrocarbons of the Benzene Series, C_nH_{2n-6}.

The compounds of this series, which commence the large class of the so-called aromatic compounds, are specifically characteristic of coal-tar. They occur also in the tar from wood, browncoal, shale, &c., but therein occupy a subordinate position‡. But they are also formed by many reactions; above all by the action of heat, partly from their own higher homologues or other derivatives, partly by the decomposition or by the molecular condensation of fatty compounds. By the action of high temperatures, *e. g.* by passing the vapour through red-hot tubes, benzene is formed not merely from toluene, xylene, styrolene, &c., but also from alcohol, acetic acid, ethylene, methane, frequently along with naphthalene; *e. g.*

$$4C_7H_8 = 3C_6H_6 + C_{10}H_8 + 6H.$$

* Zeitschr. f. Chemie (2), 1868, iv. p. 278.

† Journ. Chem. Soc. xlvii. p. 669.

‡ Markownikoff (Ann. Chem. Pharm. ccxxxiv. p. 89) has found in Caucasian petroleum large quantities of benzene, toluene, xylenes, pseudocumene, mesitylene, durene, isodurene, diethyltoluene, and other hydrocarbons of the formulæ $C_{11}H_{16}$, $C_{11}H_{12}$, $C_{12}H_{14}$, $C_{13}H_{14}$. If these discoveries, which are certainly in opposition to the assertions of all previous investigators, were confirmed, it would become doubtful how much of the aromatic hydrocarbons, found after passing petroleum residues through red-hot tubes, are newly formed, and how much was already pre-existent in the original substance.

Of course, even more highly condensed molecules, such as anthracene, phenanthrene, chrysene, &c., are formed in a similar way, hydrogen being eliminated. By passing the mixed vapours of benzene and toluene through red-hot tubes, Carnelley* obtained naphthalene, diphenyl, paratolylphenyl, orthoparadiphenyl, two methylene diphenylenes, phenanthrene, anthracene, paradiphenylbenzene, a hydrocarbon $C_{32}H_{28}$, a liquid hydrocarbon fusing at 13° and boiling at 290–316°, two other liquid hydrocarbons (or mixtures of hydrocarbons) boiling at 359–383° and 404–427°, and solid black bitumen.

It thus becomes conceivable why (as stated on p. 17) destructive distillation at lower temperatures yields more of fatty bodies and less of permanent gases, at higher temperatures more of aromatic compounds and more of permanent gases, and why, by passing the heavy hydrocarbons of the fatty class (from wood-tar, shale-tar, petroleum, &c.) through red-hot tubes, benzene and its derivatives can be prepared on a large scale (p. 90).

One of the most important parts in the formation of these bodies seems to be played by acetylene. According to Berthelot†, on heating acetylene over mercury in a bent glass tube up to the softening-point (*i. e.* to a dark red) there was produced, along with a number of secondary products occurring in small quantity, a large amount of benzene, styrolene, naphthalene, retene, &c. At a bright red heat another kind of decomposition set in; then acetylene was almost completely split up into its elements. Berthelot consequently views benzene as triacetylene, styrolene as tetracetylene, retene as enneacetylene: thus,

$$3C_2H_2 = C_6H_6, \text{ benzene;}$$
$$4C_2H_2 = C_8H_8, \text{ styrolene;}$$
$$9C_2H_2 = C_{18}H_{18}, \text{ retene; &c.}$$

The fatty bodies likewise yield acetylene under the action of heat; and Berthelot ascribes the formation of aromatic compounds, always observed in this case, to the secondary condensation of acetylene by itself and with other compounds.

Similar conclusions are arrived at by O. Jacobsen‡, who, besides

* Journ. Chem. Soc. Nov. 1880, p. 701.
† Compt. Rend. lxii. pp. 905, 947.
‡ Ber. deutsche chem. Ges. 1877, p. 853.

acetylene, assumes its next homologue, allylene, C_3H_4, to participate in the synthesis. This is shown by these equations:

$$\begin{aligned} 3C_2H_2 &= C_6H_6, \text{ benzene;} \\ 2C_2H_2 + C_3H_4 &= C_7H_8, \text{ toluene;} \\ C_2H_2 + 2C_3H_4 &= C_8H_{10}, \text{ xylenes (three);} \\ 3C_3H_4 &= C_9H_{12}, \text{ mesitylene and pseudocumene.} \end{aligned}$$

This hypothesis would explain why,

1st, besides benzene, only those homologues occur the lateral chains of which consist of methyl*;

2nd, the methylbenzenes found in tar-oil do not extend beyond the tri-derivatives;

3rd, of all possible tri-derivatives only mesitylene and pseudocumene are present;

4th, all three xylenes occur in tar-oil.

(The last is made clear by the graphic reaction schemes given in the original.)

Allylene has not yet been observed among the products of destructive distillation; but Jacobsen ascribes this to its easier condensation, and to the difficulty of discovering small quantities of it mixed with acetylene.

Even on Jacobsen's theory the formation of the other hydrocarbons occurring in tar can only be explained by elimination of hydrogen, as shown by Anschütz†:

$$\begin{aligned} 5C_2H_2 &= C_{10}H_8 + 2H \\ C_{10}H_8 + 2C_2H_2 &= C_{14}H_{10} + 2H. \end{aligned}$$

Anthracene and phenanthrene might also be formed by a condensation of ditoluene:

$$2C_7H_8 = C_{14}H_{10} + 6H.$$

It is an argument in favour of Jacobsen's theory, that tar has certainly been found to contain only methylated benzene homologues, exactly those mentioned by him, but neither cumene (isopropylbenzene), nor propylbenzene, nor ethylmethylbenzene.

* Jacobsen himself has had to modify this part of his theory. In the 'Berichte,' 1886, p. 2515, he declares it to be proved that coal-tar contains benzene substitution-products with longer lateral chains, but he was not able to obtain these in sufficient quantity to identify them.

† Ber. deutsch. chem. Ges. 1878, p. 1215.

It is true that older treatises enumerate cymene (methyl-isopropylbenzene) as a constituent of tar, but upon insufficient evidence; so that nowadays cymene is not considered to be present in tar. But since K. E. Schulze has discovered tetramethylbenzene in coal-tar, Jacobsen's theory can no longer be upheld without some modification. K. E. Schulze himself* has originated another theory on the formation of the hydrocarbons found in coal-tar. He believes the phenols to be the primary products, and the hydrocarbons to be formed from them by the splitting-off of the elements of water (comp. p. 89).

Benzene, C_6H_6.

Syn. benzol (this word is now mostly used for the commercial mixture of benzene, toluene, &c. in varying quantity), phenylic hydride. It was discovered in 1825, by Faraday, in the liquid separating from condensed oil-gas. Mitscherlich, in 1833, prepared it by the dry distillation of calcium benzoate, determined its empirical formula, and conferred upon it its present name; he also discovered nitrobenzene. Its first discovery in coal-tar is claimed by Leigh, who states that his communication to that effect made to the British Association meeting in 1842 was omitted to be mentioned in its Report by an oversight†. At all events that observation remained unknown and sterile; and the credit of having, in 1845, distinctly recognized the presence of benzene in coal-tar, and proved it by transforming it into nitrobenzene and aniline, will not be denied to A. W. Hofmann‡. The process for obtaining it in any quantity from coal-tar was worked out in his laboratory by one of his pupils, Charles Mansfield§, who carried out the process on the large scale and minutely described the principle of dephlegmation for separating the various hydrocarbons; he distinctly pointed out that the apparatus employed in rectifying spirit might be employed for this purpose, even with greater advantage than for spirit of wine itself‖—a suggestion usually, but erroneously, stated to be due to E. Kopp, who first speaks of it in 1860¶. Mansfield fell a victim to his discovery. On

* Ann. Chem. Pharm. vol. ccxxvii. p. 143.
† Moniteur Scientif. 1865, p. 446.
‡ Ann. Chem. Pharm. liv. p. 204.
§ Engl. Patent No. 11,260, of Nov. 11, 1847; Q. J. Chem. Soc. i. p. 244.
‖ Lecture at the Royal Institution, April 27, 1849.
¶ Moniteur Scientif. 1860, vol. ii. p. 829.

the 17th of February, 1854, he was occupied with the distillation of benzene on a somewhat large scale for the Paris Exhibition, when the liquid in the retort boiled over and took fire, burning him so severely that he died in a few days.

Mansfield already utilized the property possessed by benzene (observed first by Faraday), of crystallizing at 0°, for preparing it in a state of perfect purity. It is allowed to freeze in a freezing-mixture; the liquid portion is pressed out; and, if necessary, the operation is repeated. Hofmann * has shown that the crystals easily enclose mother-liquor, which causes the product to contain toluene. Hence he prescribes preventing the formation of large crystals and completely separating the mother-liquor by atmospheric pressure, for which purpose he describes a convenient laboratory-apparatus.

Benzene is formed, on the one hand, by synthesis (condensation) from acetylene and other fatty compounds of simpler molecular constitution, and, on the other, by the splitting-up of more complex compounds, both fatty and aromatic, in both cases by the action of strong heat. In sealed tubes it remains unchanged even when heated to 400° C. Hence it is one of the most stable organic compounds; but on passing through red-hot tubes it also is decomposed, more highly condensed hydrocarbons, especially diphenyl, being formed (Berthelot, Schulze †, Schmidt ‡, Behr und von Dorp §). Passed through red-hot tubes along with ethylene, it yields styrolene, naphthalene, diphenyl, acenaphthene, anthracene, &c. (Berthelot), all of which must consequently be found in crude illuminating-gas and the tar therefrom.

Benzene is a colourless mobile liquid of peculiar smell. Its boiling-point is stated at 80–81° (Mansfield), 80°·4 at a pressure of 760 millim. (Kopp), 80°·1 (Warren), 80°·36 (Regnault). Adrieenz ‖ found that benzene prepared from tar boils at 80°·53–80°·62, that from benzoic acid at 80°·60–80°·67. The temperature of a boiling mixture of benzene and water is 68°·5, that of the mixed vapours 69°·1 ¶. At 0° it solidifies to a mass of crystals, which fuse at 4°·45 (Regnault) or 7° (Mitscherlich). The crystals are

* Ber. deutsch. chem. Ges. 1871, p. 162.
† Ann. Chem. clxxiv. p. 201.
‡ Ber. deutsch. chem. Ges. 1874, p. 1365. § Ibid. 1873, p. 723.
‖ Ibid. 1873, p. 441.
¶ Naumann, Ber. deutsch. chem. Ges. 1877, p. 142.

orthorhombic prisms, whose axes $a : b : c$ have the ratio 0·891 : 1 : 0·799 *. Its specific gravity at 0° = 0·8991 (Kopp), at 15° = 0·884 (Mendelejeff); at 0° = 0·8957, at 15° = 0·8820 (Warren). Its coefficient of expansion is stated by Kopp for the temperature $t°$ (between 11°·4 and 81°·4) to be

$$V_t = 1 + 0{\cdot}001171626t + 0{\cdot}00000127755t^2 + 0{\cdot}0000000080648t^3.$$

Adrieenz gives the following table for the specific gravity of benzene (from benzoic acid) :—

Temp.	Sp. gr.	Volume.	Temp.	Sp. gr.	Volume.
°			°		
0	0·90023	1	45	0·85291	1·05550
5	0·89502	1·00582	50	0·84748	1·06228
10	0·88982	1·01169	55	0·84198	1·06924
15	0·88462	1·01764	60	0·83642	1·07637
20	0·87940	1·02367	65	0·83078	1·08370
25	0·87417	1·02979	70	0·82505	1·09123
30	0·86891	1·03603	75	0·81923	1·09898
35	0·86362	1·04238	80	0·81331	1·10696
40	0·85829	1·04887			

The specific gravity of benzene from tar-oil he found at 0° = 0·90122 and 0·90129.

The specific heat of benzene between 19° and 46° = 0·450 (Kopp). Its refraction-index † for the line A is 1·4593; for D it is 1·5050; and for H, 1·5307; Adrieenz gives 1·4957 at 15°·2 for D.

Benzene is not merely a most important substance for industrial purposes, but even more so for theoretical chemistry. The enormous array of aromatic compounds are all derived from benzene. It would seem well-nigh impossible to find one's way through this interminable field, if Kekulé's celebrated theory of the constitution of benzene had not brought light and order into it. It can be stated without fear of contradiction, that without Kekulé's hexagon formula nothing like so many and so important aromatic compounds would have been discovered as there have been; his hypothesis is certainly one of the most fertile and suggestive that have ever been propounded in Chemistry.

Nearly all chemists agree with Kekulé in assuming that the six carbon atoms of benzene are united in a closed chain (nucleus),

* Groth, Pogg. Ann. cxli. p. 31.

† Gladstone, Chem. Soc. Journ. 1870, vol. xxiii. p. 152.

and that, of the four bonds of each atom, three are satisfied by other carbon atoms of the same nucleus, the fourth being satisfied by hydrogen atoms. But opinions differ on the special kind of bond; and it does not seem the place here to enter into this theoretical discussion, which is not yet brought to a close.

For the sake of simplicity, benzene is usually represented merely by the figure of a hexagon, and its derivatives by attaching the respective groups to the corners, whilst the empty corners are understood to be filled with hydrogen atoms.

Benzene is very little soluble in water, but sufficiently so to communicate its smell. It is easily soluble in alcohol, ether, wood-spirit, acetone, &c. It dissolves iodine, sulphur*, phosphorus (when hot), and (very easily) fats, ethereal oils, resins, &c. It is easily inflammable, as well as its vapour, which necessitates great precaution in storing it in quantity. It burns with a strongly smoking flame. Ordinary coal-gas passed through benzene gains very much in illuminating-power; Berthelot even ascribes that of (Paris) lighting-gas essentially to the benzene contained in it, whilst formerly substances of the ethylene series received the credit. This has been confirmed by the researches of Frankland, of Knoblauch†, &c., and is now pretty generally assumed to be correct. Even atmospheric air passed through benzene yields a mixture burning with a bright flame, upon which property Mansfield at that time (before the discovery of the aniline colours) founded his hopes of an industrial utilization of benzene. Frankland and Thorne‡ have made a quantitative investigation of the illuminating-power of benzene when mixed in the state of vapour with nonluminous gases.

Benzene, on being inspirated in breathing, causes first a quickening of the pulse and the respiration, afterwards stupefaction, and in large doses (*e. g.* 50 g. for a cat) it produces death. In the case of men, the inspiration of 10 grammes benzene causes headache, giddiness, inclination to vomiting, coughing, and sleepiness. 40 to 50 grammes produce anæsthesia, similar to that produced by chloroform, with violent perspiration, sometimes with

* The somewhat considerable solubility of sulphur in benzene and ether (also the heavy tar-oils) has been studied in detail by E. Pelouze, junior (Compt. Rend. lxviii. p. 1179, lxix. p. 56).

† Ber. deutsch. chem. Ges. 1881, p. 240.

‡ Chem. News, xxxvii. pp. 36, 72.

all the appearances of drunkenness. The workmen often complain of "ant-creeping" and dryness of the skin, owing to the oily secretions of the skin being dissolved. For all that, the men working in india-rubber works, and continually exposed to benzene vapours, enjoy normal health.

The changes undergone by benzene when passed through red-hot tubes have been mentioned above (p. 115).

Concentrated sulphuric acid at the ordinary temperature acts very little upon benzene, for which reason the latter can be purified by treatment with that acid. Even then, ordinary benzene contains some thiophen (see below), which can be removed by more energetically agitating with strong sulphuric acid till the "indophenine reaction," that is, a blue colour imparted to isatin, is no longer yielded (V. Meyer). But on heating benzene monosulphonic acid ($C_6H_5 . SO_3H$) is formed, and at very high temperatures, or more easily by fuming sulphuric acid, benzene disulphonic acid ($C_6H_4(SO_3H)_2$). Concentrated nitric acid converts benzene into nitro-compounds (mono- and dinitrobenzene), upon which its detection, its estimation, and, to a great extent, its industrial application are based. Oxidizing reagents, such as potassium permanganate, manganese dioxide, chromic acid, &c., act upon it but little and with formation of complex products. Chlorine and bromine yield with it addition and substitution products.

Toluene, $C_7H_8 = C_6H_5 . CH_3$.

Syn. methylbenzene. It was discovered, in 1838, by Pelletier and Walter, in the condensation-products from the manufacture of rosin-gas, and was called "retinaphtha." Afterwards Deville obtained it by destructive distillation of tolu balsam; the name of toluene (toluol) was given to it by Berzelius. Mansfield found it in coal-tar; and it has since been met with in many mineral oils. Its formation, together with that of analogous compounds, has been mentioned above. It is obtained from coal-tar in very large quantities, and if necessary in a state of great purity, and is largely employed, partly for the manufacture of colouring-matters, partly as a solvent. It is more difficult to prepare in a perfectly pure state than benzene, because it does not crystallize.

The received theory admits only one toluene; and in fact it has

been proved by Berthelot* and Rosenstiehl† that all toluenes, whatever may be their origin, are identical.

Toluene is a colourless, mobile, strongly refractive liquid. Its boiling-point is 110° (Wilson), or 111° (Wilbrand and Beilstein), or 110°·3 (Warren). It does not solidify at −20°. Its specific gravity at 0° =0·8824, at 15° =0·8720 (Warren); or at 0° =0·8841, at 15° =0·8702 (Louguinine). The latter states its volume at the temperature t, if at 0°=1, as

$$V_t = 1 + 0{\cdot}001028t + 0{\cdot}000001779t^2.$$

Deville gives 1·4899 as its refraction-index.

The smell of toluene is rather different from that of benzene. It is insoluble in water, but communicates its smell to it; it is miscible with alcohol, ether, carbon bisulphide, &c. It dissolves sulphur, phosphorus, iodine, fats, &c. When ignited, it burns with a bright and strongly smoking flame. Passed through red-hot tubes it yields benzene, naphthalene, anthracene, phenanthrene, &c.

According to Berthelot, toluene possesses, similarly to oil of turpentine, the property of rendering oxygen active; when toluene is shaken up with a very dilute tepid solution of indigo in the presence of air, decolorization takes place. [This statement seems to require confirmation. Watson Smith has many times tried the experiment, but never succeeded.]

Concentrated sulphuric acid dissolves toluene on heating and prolonged shaking; fuming acid does so much more quickly. In this two isomeric sulphonic acids are formed. Nitric acid of less than 1·42 sp. gr. does not act upon it when cold; but fuming nitric acid does so violently, even more so than upon benzene, nitro-products up to trinitrotoluene being formed. Oxidizing agents (dilute nitric acid, chromic acid, potassium permanganate) convert it into benzoic acid, but only with difficulty and great loss, so that this direct oxidation is scarcely practised on an industrial scale.

Xylenes, $C_8H_{10}=C_6H_4(CH_3)_2$.

Syn. dimethylbenzene. Xylene (*i. e.* a mixture of the isomers) was discovered in 1850, by Cahours, in crude wood-naphtha. In coal-tar it was found by Ritthausen and Church. Latterly it has

* Bull. Soc. Chim. 1869, xi. p. 381. † Ibid. xi. p. 385.

been synthetically produced by Friedel and Craffts, by treating benzene or toluene with methylic chloride in the presence of aluminium chloride.

Fittig first proved in 1869* that coal-tar xylene is not a homogeneous body; he stated it to contain 90 per cent. metaxylene and 10 paraxylene. But O. Jacobsen† has proved the presence of orthoxylene, and estimates the proportion at 70–75 per cent. metaxylene, 20–25 paraxylene, and 10–15 orthoxylene; in any case different tars will differ in this respect (comp. Chap. XII.).

Crude xylene, that is xylene which has not been treated with sulphuric acid (by which considerable quantities of orthoxylene must be dissolved), must contain much more orthoxylene than was found by Jacobsen in the refined article examined by him. This supposition (thrown out by the author in the first edition of this work, p. 44) has been confirmed by Jacobsen‡, who found up to 25 per cent. of orthoxylene in crude coal-tar xylene.

Orthoxylene, $C_6H_4\begin{matrix}-CH_3\,(1)\\-CH_3\,(2)\end{matrix}$, is a colourless liquid, whose pleasant aromatic smell differs from that of its isomers. It boils at 141–142°, and is not yet solid at −22°. It dissolves in concentrated sulphuric acid, forming *one* sulphonic acid. Dilute nitric acid forms orthotoluylic acid, fusing at 102°; potassium permanganate forms phthalic acid; chromic acid entirely burns it up. The sulphochloride melts at 52°, the sulphamide at 144°.

Metaxylene (*syn.* isoxylene), $C_6H_4\begin{matrix}-CH_3\,(1)\\-CH_3\,(3)\end{matrix}$, boils at 139°, is also soluble in concentrated sulphuric acid, two sulphonic acids being formed. Dilute nitric acid forms metatoluylic acid, of 106° fusing-point; potassium permanganate and chromic acid form isophthalic acid. There are two sulphochlorides, one melting at 34°, the other liquid; the two sulphamides melt at 137° and 96° respectively. Specific gravity of metaxylene = 0·8668 at 19°.

Paraxylene, $C_6H_4\begin{matrix}-CH_3\,(1)\\-CH_3\,(4)\end{matrix}$, melts at 15°, and boils at 137°·5–138°. Possesses an odour similar to that of orthoxylene, but with a faint smell of aniseed superadded. According to Glinzer and

* Ann. der Chemie, cliii. p. 265.
† Ber. deutsch. chem. Ges. 1877, p. 1009.
‡ Berichte, 1881, p. 2628.

Fittig, its sp. gr. (not quite pure) at 18°·5=0·8625. It is very little acted upon even by hot concentrated sulphuric acid; but faintly fuming oil of vitriol dissolves it, forming a sulphonic acid which can be precipitated by water and purified by recrystallization, and from which by dry distillation pure paraxylene is regenerated. This behaviour shows how it can be isolated. Dilute nitric acid forms paratoluylic acid, melting at 178°; potassium permanganate and chromic acid form terephthalic acid. The sulphochloride melts at 26°, the sulphamide at 148°. The tar isomers dissolved in sulphuric acid can be separated in the following way (Jacobsen). As much as possible of the excess of sulphuric acid is removed by calcium carbonate; the liquid is mixed with a slight excess of sodium carbonate, and the filtrate evaporated so far that on cooling a considerable crop of salt is obtained. This sodium orthoxylene sulphonate can be purified by recrystallization, whilst the mother liquors contain sodium metaxylene sulphonate. From these salts the hydrocarbons are obtained by dry distillation or by heating with hydrochloric acid to 195°. Coal-tar xylene contains a body similar to paraffin, insoluble even in fuming oil of vitriol, which has not yet been examined (compare Levinstein's process in the 12th Chapter).

Trimethylbenzenes, $C_9H_{12}=C_6H_3(CH_3)_3$.

Mansfield originally discovered hydrocarbons of the empirical formula C_9H_{12} in coal-tar, but evidently did not isolate them in the pure state. Like him, other chemists for a number of years believed they had to do with a homogeneous body, identical with the retinyl obtained in 1837 by Pelletier and Walter from rosin-oil or cumene (cumol, propylbenzene), obtained by Gerhardt and Cahours from cuminic acid. Frequently even xylene was confounded with cumene. This confusion Beilstein * put an end to by describing the individual substance as *pseudocumene*. Already Warren† had obtained it in a similar state, boiling at 169°·8. But Fittig and his disciples ‡ proved that Beilstein's pseudocumene is a mixture of two isomeric trimethylbenzenes, viz. that of pseudocumene, in the present sense of the term (1, 2, 4), and of mesitylene

* Ann. Chem. Pharm. cxxxiii. p. 32.

† Chem. News, xii. p. 292.

‡ Ann. Chem. Pharm. cxxxix. p. 184; cxlv. p. 137; cl. pp. 257, 283, 292.

(1, 3, 5). Besides them O. Jacobsen * has found a paraffin, $C_{10}H_{22}$, boiling at 170–171°. The same chemist has described † the preparation of both hydrocarbons in a pure state by converting them into their sulphamides, separating these by crystallizing from alcohol, and decomposing the sulphamides by heating them with hydrochloric acid to 175°.

Engler‡ has found both pseudocumene and mesitylene in different descriptions of petroleum; so has Markownikoff (p. 111, note).

Pseudocumene, $C_6H_3\begin{cases}CH_3\,(1)\\CH_3\,(2)\\CH_3\,(4)\end{cases}$, boils at 169°·5§. Its smell differs from that of the lower homologues. It is insoluble in water, soluble in ether and alcohol, also in glacial acetic acid (like mesitylene). Treated with sulphuric acid it dissolves (like mesitylene) with formation of a sulphonic acid.

Mesitylene, $C_6H_3\begin{cases}CH_3\,(1)\\CH_3\,(3)\\CH_3\,(5)\end{cases}$, discovered by Kane‖ by treating acetone with sulphuric acid, by Fittig in coal-tar oil. Boils at 163° (Fittig); smells rather like garlic.

Hemellithol, $C_6H_3\begin{cases}CH_3\,(1)\\CH_3\,(2)\\CH_3\,(3)\end{cases}$, discovered by O. Jacobsen in 1882 (Berl. Ber. 1882, p. 1857), and found by him in coal-tar oils in 1886 (*ibid.* 1886, p. 2517). Boils at 175–175°·5, and does not solidify at −20°.

Tetramethylbenzenes, $C_{10}H_{14}$.

K. E. Schulze¶ found the 1, 2, 4, 5 *Durene* in the fraction of tar-oil boiling between 180° and 200°, after removing the bases and phenols. White scales, with a faint fluorescence, smelling similar to pseudocumene; fusing-point 80–81°, boils at 196°; sublimes with much more difficulty than naphthalene. Most probably other isomers are present in this oil, which occurs in coal-tar in nearly the same proportion as benzene.

ADDITION-PRODUCTS of the benzene series have been mentioned on p. 109.

* Ann. d. Chemie, clxxxiv. p. 179.
† Ber. deutsch. chem. Ges. 1876, p. 256.
‡ Ibid. 1885, p. 2234.
§ O. Jacobsen, Berl. Ber. 1886, p. 2513.
‖ Poggend. Ann. xliv. p. 474.
¶ Ber. deutsch. chem. Ges. 1885, p. 3032.

Styrolene, $C_8H_8=C_6H_5.CH=CH_2$.

Syn. cinnamene, phenylethylene. Usually obtained from storax or Peru balsam; synthetically by Berthelot* by condensation of acetylene at the temperature of softening glass, or, better, by passing a mixture of benzene and ethylene through red-hot, and even better through white-hot tubes, thus:

$$C_6H_6+C_2H_4=C_8H_8+H_2.$$

These reactions explain the occurrence of styrolene in coal-tar, in which, however, it occurs only in insignificant quantities.

It is a colourless mobile oil, with a strong aromatic smell, reminding one of benzene and naphthalene. It does not solidify at $-20°$, boils at 145°, but volatilizes at ordinary temperatures, so that it does not leave a grease-spot on paper. Sp. gr. at $16°=0{\cdot}876$. Its solubilities are quite analogous to those of benzene. Caustic potash has no action upon it; fuming sulphuric acid converts it into a sulphonic acid, ordinary sulphuric acid only into a solid polymer, which, on distillation, is reconverted into styrolene. Chlorine and bromine unite directly with it. Fuming nitric acid dissolves it, forming a nitro-compound. At a red heat it splits up into benzene and acetylene,

$$C_8H_8=C_6H_6+C_2H_2,$$

or, if mixed with hydrogen, into benzene and ethylene,

$$C_8H_8+H_2=C_6H_6+C_2H_4;$$

that is, the reaction is the inverse of that which took place in its formation. Heated with ethylene it yields benzene and naphthalene; heated with benzene, naphthalene and anthracene. It probably plays an important part in the formation of these higher hydrocarbons, and, for that very reason, does not occur in large quantities in coal-tar.

Styrolene hydride, C_8H_{10}.

?

Naphthalene, $C_{10}H_8$.

Discovered by Garden in 1820; first studied in detail by Laurent. It is formed in innumerable cases by the action of heat

* Compt. Rend. lxiii. pp. 481, 518, 792, 834; lxviii. p. 327.

on organic substances, but only at rather high temperatures; so that tar obtained at a comparatively low heat does not contain it at all. In gas-tar it always occurs, but in very varying quantities, very much greater since the cast-iron retorts have been replaced by fireclay retorts worked at much higher temperatures. The statement of Calvert*, that Newcastle tar contains 58 per cent. of naphthalene, is absurd on the face of it; ordinarily tar rarely contains more than from 5 to 10 per cent. The mode of its formation has been explained on pp. 113 & 115.

In the pure state it forms white crystalline masses or thin rhomboidal scales; on spontaneous evaporation of an ethereal solution it appears in monoclinic prisms (Laurent). It fuses at 79°; the statements respecting its boiling-point vary between 212° and 220°; but 218° seems to be the correct figure. Sp. gr. at 15°=1·1517, at 18°=1·158, at 79°·2=0·9778, at 100°=0·9628 (compared with water at 0°). Melted naphthalene, according to Vohl †, absorbs a large quantity of air, which is given off again on cooling; it is said to be much richer in oxygen than atmospheric air. Naphthalene volatilizes far below its boiling-point, and distils both with aqueous vapour and with that of light tar-oils; hence it always appears with the latter in crude tar-oils. In an ammoniacal atmosphere it volatilizes more easily than in air, hydrogen, &c. ‡ Even at ordinary temperatures it volatilizes slowly and gives off a penetrating tarry smell, which clings a long time to clothes &c., and is said to keep off moths and other vermin. Ballo § asserts that this smell is not that of pure naphthalene, but of leucoline oil; however, the purest obtainable naphthalene exhales it quite strongly. Its taste is pungent. It burns with a strongly smoking flame, but its vapour mixed in small quantity with gas considerably enhances the illuminating-power of the latter.

It is insoluble in cold || but not quite so in hot water; so that the latter turns milky on cooling. It is easily soluble in alcohol, ether, fatty and essential oils, and acetic acid, very much so in phenols, but less easily in the indifferent tar-oils. When melted it dissolves phosphorus, sulphur, indigo, and several metallic sul-

* Compt. Rend. xlix. p. 262. † Journ. f. prakt. Chem. cii. p. 29.

‡ Tieftrunck, Ber. d. chem. Ges. 1878, p. 1466.

§ Dingler's Journ. ccii. p. 377.

|| Lupton (Chem. News, xxxiii. p. 90) doubts this, but does not adduce any positive proof to the contrary.

phides, which crystallize on cooling. According to Bechi *, 100 parts of absolute alcohol at 15° dissolve 5·29 parts, at the boiling-point any quantity; 100 parts of toluene at 16°·5 31·94 parts, at 100° any quantity.

Alkalis do not act very much upon naphthalene, but alkaline liquors dissolve a little of it. Concentrated sulphuric acid, on heating, converts it into sulphonic acids—below 70° principally into the *a*, at 160° almost entirely into the *β* modification. This behaviour is very important, because the corresponding naphthols can only be made from the proper sulphonic acids. Chlorine yields both addition and substitution products; nitric acid, nitronaphthalene.

The constitution of naphthalene has been elucidated chiefly by the researches of Erlenmeyer † and Graebe ‡; it is generally assumed to consist of two benzene nuclei, attached to each other by two carbon atoms.

In order to prove the presence of naphthalene, Vohl treats the substance in question with fuming nitric acid, adds a large quantity of water, washes the precipitated nitro-compound, and puts it into a boiling mixture of 1 part potassium monosulphide and 1 part caustic potash; traces of naphthalene yield a beautiful purple solution.

Naphthalene dihydride, $C_{10}H_{10}$.

Discovered by Berthelot § as a product of the action of concentrated hydriodic acid on naphthalene; occurs also in coal-tar. A viscid fluid, with a strong, disagreeable smell, boiling at 200–210°. Is powerfully acted upon by bromine, and dissolves in cold fuming nitric acid.

Naphthalene tetrahydride, $C_{10}H_{12}$.

Occurs in small quantity along with the dihydride; it boils at 190°. Its other properties are similar to those of the latter body.

Methylnaphthalenes, $C_{11}H_{10}$.

Reingruber || found these in that portion of coal-tar which distils between 220° and 270°, and which remains liquid at ordinary

* Ber. deutsch. chem. Ges. 1879, p. 1928.
† Ann. Chem. Pharm. cxxxvii. p. 346.
‡ Zeitschr. f. Chemie [2], iv. p. 114.
§ Bull. Soc. Chim. 1868, ix. p. 287.
|| Ann. Chem. ccvi. p. 367.

temperatures; but the two isomeric methylnaphthalenes were only separated by K. E. Schulze (Ber. d. chem. Ges. 1884, p. 842). They are miscible in all proportions with absolute alcohol, ether, benzene, carbon bisulphide, and glacial acetic acid. Oxidizing agents act briskly upon them, and destroy them with evolution of carbon dioxide.

α Methylnaphthalene is a colourless oil of an aromatic smell, with strong refraction, but in the pure state without fluorescence. It remains liquid at −18° and boils at 240–243°; sp. gr. 1·0287 at 11°·5.

β Methylnaphthalene crystallizes in scales somewhat like naphthalene, of rather pungent smell and burning taste; it melts at 32°·5, and boils at 241–242°.

The ordinary "creosote oil" of trade, which distils mainly between 200° and 300°, contains about 6 per cent. of these methylnaphthalenes, rather more of the β than of the α modification.

Dimethylnaphthalene, $C_{12}H_{12}$.

Emmert and Reingruber* found a body of this composition, boiling at 262–264°, in coal-tar. There are evidently several isomeric bodies of this formula, but so far it has not been found practicable to separate them.

Acenaphthene, $C_{12}H_{10}$.

Occurs in that portion of coal-tar which boils at 270–300°, especially between 280° and 290°, and crystallizes on cooling. By recrystallizing from light tar-oil or alcohol, or cautious subliming, it is obtained pure†. It fuses at 95° and boils at 277°·5. Crystallized from alcohol it forms long, colourless, shining needles; from heavy tar-oils it separates in hard, brittle crystals. Its smell resembles that of naphthalene. It is little soluble in cold, easily in boiling alcohol. Bromine acts readily upon it; concentrated sulphuric acid dissolves it, forming a sulphonic acid, of which all the salts are easily soluble; concentrated nitric acid forms a nitro-compound. Its constitution is $C_{10}H_6\begin{matrix}CH_2\\|\\CH_2\end{matrix}$.

* Ann. d. Chem. ccxi. p. 65.

† Berthelot, Ann. Chim. Phys. [4] xii. p. 226.

Acenaphthene hydride, $C_{12}H_{12}$.

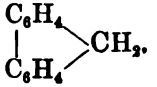
Is stated by Berthelot to occur along with the preceding body in coal-tar. It boils at 260°.

Diphenyl, $C_{12}H_{10}$.

Discovered in 1862 by Fittig *. It occurs in that fraction of coal-tar which boils at from 220° to 270°†; this has been confirmed by K. E. Schulze (B. d. chem. Ges. 1885, p. 1203), who considers it also probable that higher homologues (methyldiphenyl) occur there as well. It fuses at 70°·5, and boils at 254°. It readily dissolves in alcohol and ether, and crystallizes in large colourless scales. Bromine, sulphuric acid, and nitric acid act upon it, and form corresponding derivatives. Its rational formula is C_6H_5—C_6H_5. It bears a close relationship to phenanthrene.

Fluorene, $C_{13}H_{10}$.

Syn. diphenylene-methane. Prepared by Berthelot‡ from coal-tar, synthetically by Graebe, Fittig, and others in various ways; specially examined by Barbier§. It is obtained from the fraction of coal-tar boiling between 290° and 350°, after naphthalene and anthracene are separated by fractional distillation; the portion distilling between 295° and 310° is purified by repeated recrystallization from alcohol. It forms colourless scaly crystals with a violet fluorescence, little soluble in cold, easily in hot alcohol, also in ether, benzene, and carbon bisulphide. Fuses at 113°, boils at 295°, but volatilizes with aqueous vapour. Bromine and nitric acid yield derivatives with it. The rational formula is



There is a series of isomers of this formula || which are probably partly contained in coal-tar.

* Ann. Chem. Pharm. cxxi. p. 361.

† Fittig and Büchner, Ber. deutsch. chem. Ges. 1875, p. 22.

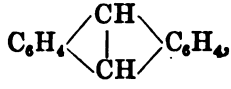
‡ Compt. Rend. lxv. p. 465.

§ Compt. Rend. lxxvii. p. 442; lxxix. p. 1151.

|| Carnelley, Journ. Chem. Soc. Nov. 1880, p. 701; Lunge and Steinkauler, Ber. deutsch. chem. Ges. 1880, p. 1656.

Anthracene, $C_{14}H_{10}$.

Discovered by Dumas and Laurent in 1832, and described as *paranaphthalene*; more specially examined in 1857 by Fritzsche, who was the first to find it in coal-tar *. This was confirmed by Anderson's extended investigation in 1862. Anderson also established the correct formula of anthracene. Synthetically it was first prepared by Limpricht † in 1866, from benzylic chloride, in the same year by Berthelot, pyrogenetically, from simpler hydrocarbons. The most momentous epoch in its history was marked by Graebe and Liebermann's discovery, in 1868, that it is formed from alizarin by the reducing action of zinc dust, and that alizarin can be synthesized from it ‡. The same chemists established the structural formula of anthracene, but first gave it that now generally ascribed to phenanthrene. Anthracene is now universally represented thus,



i. e. two benzene nuclei, connected by two carbon atoms which are united with each other by another bond. It is also now ascertained that both bonds are in the ortho-position towards the benzene nuclei.

Anthracene is formed in many cases when organic bodies are subjected to a great heat, not merely in the dry distillation of coal, but also when passing the vapours of petroleum, browncoal-tar, wood-tar, benzene, spirits of turpentine, &c. through red-hot tubes.

The mode of its formation from other hydrocarbons is illustrated by the following equations, which may serve as examples :—

$$\underset{\text{Toluene.}}{2C_7H_8} = C_{14}H_{10} + 6H$$

$$\underset{\text{naphthalene + acetylene.}}{C_{10}H_8 + 2C_2H_2} = C_{14}H_{10} + 2H$$

&c. &c.

* Journ. prakt. Chem. lxxiii. p. 286.
† Ann. Chem. Pharm. cxxxix. p. 308.
‡ Berichte, 1868, p. 49.

Köhler* found 35 per cent. anthracene in a product accidentally formed by a violent reaction on overheating the higher-boiling fractions of crude carbolic acid, although that product had been obtained from "light oil," and could hardly contain substances which would yield anthracene by a mere splitting-off of the elements of water. He regards this as a confirmation of K. E. Schulze's theory of the formation of the hydrocarbons of tar from phenols, and at the same time of the view that the anthracene of coal-tar is for the most part formed during the process of distillation itself.

Anthracene has also been found in that peculiar greasy substance called "stupp," which is formed in the distillation of mercury from its ores (G. Goldschmidt and M. von Schmidt).

Its preparation from the highest-boiling constituents of coal-tar, and the analysis of crude anthracene, will be minutely described in Chapter VII. The preparation of chemically pure anthracene (which is not a commercial article) is not easy, unless crude anthracene distilled over caustic potash can be employed. From this, by one washing with carbon disulphide and several recrystallizations from petroleum spirit and benzene, beautiful white scales with blue fluorescence are obtained, which it is very difficult to obtain from ordinary crude anthracene. This is best accomplished after subliming at the lowest possible temperature and washing with ether to remove yellow colouring-matters; or it is dissolved in benzene and bleached by sunlight, in which case a little paranthracene is always formed. The safest way to obtain chemically pure anthracene is to reduce its derivatives by zinc dust †.

Pure anthracene forms shining white scales (clinorhombic prisms) with violet fluorescence. It fuses at 210° (Fritzsche, Berthelot) or 213° (Graebe and Liebermann), and sublimes at about the same temperature, with a pungent smell, yielding small, mica-like scales. At about 360° (certainly above phenanthrene) it boils and yields a yellowish-white crystalline distillate; a portion, however, is always decomposed.

Pure anthracene is insoluble in water, little soluble in alcohol, more so in ether, benzene, and essential oils, as well as in boiling alcohol, and especially in light tar-oils. According to Gessert‡,

* Ber. deutsch. chem. Gesellsch. 1885, p. 859.

† Auerbach, Das Anthracen, 2nd edit. p. 12.

‡ Dingler's Journal, cxcvi. p. 543.

100 parts of

Alcohol cold	dissolve	0·6	of anthracene,
Benzene	„	0·9	„
Carbon disulphide	„	1·7	„

According to Versmann *, at 15° 100 parts of

Alcohol, sp. gr.	0·800,	dissolve	0·591	part of	anthracene;
„ „	0·825,	„	0·574	„	„
„ „	0·830,	„	0·491	„	„
„ „	0·835,	„	0·475	„	„
„ „	0·840,	„	0·460	„	„
„ „	0·850,	„	0·423	„	„
Ether		„	1·175	„	„
Chloroform		„	1·736	„	„
Carbon disulphide		„	1·478	„	„
Glacial acetic acid		„	0·444	„	„
Benzene		„	1·668	„	„
Petroleum		„	0·394	„	„

According to Bechi †, 100 parts of

Abs. alcohol at 16° dissolve 0·076; when boiling, 0·83 anthracene;
Toluene „ 16°·5 „ 0·92; at 100°, 12·94 „

Its solution in benzene, when exposed to sunlight, soon deposits crystals of *paranthracene* which resist the action of solvents and concentrated acids and fuse at 244°, being reconverted into anthracene. Ordinary sulphuric acid with gentle heating dissolves anthracene and becomes of a greenish colour; at a higher temperature sulphonic acids are formed. Fuming sulphuric acid acts violently upon it. Oxidizing agents convert it into anthraquinone; reducing agents into hydrocarbons richer in hydrogen; nitric acid into nitro-compounds. Dissolved in benzene, along with picric acid, it yields ruby-coloured crystals, fusing at 170° and decomposed by alcohol. With dinitroanthraquinone (Fritzsche's reagent) it gives shining, rhomboidal, purple plates: if it is not quite pure, the plates are blue; if too impure, the reaction fails altogether ‡.

* Chem. News, xxx. p. 204. His anthracene probably was not quite pure.
† Ber. deutsch. chem. Ges. 1879, p. 1978.
‡ Fritzsche, Zeitschr. f. Chemie [2], iii. p. 289.

Anthracene dihydride, $C_{14}H_{12}$.

Prepared by Graebe and Liebermann*; occurs in coal-tar; crystallizes in colourless plates, similar to naphthalene; fuses at 106°, begins to sublime at the same temperature, and distils at 305° without decomposition. It volatilizes with aqueous or alcoholic vapours. It has a peculiar smell, especially at a higher temperature. It is insoluble in water, easily soluble in alcohol, ether, and benzene. In the solid state it shows no fluorescence; but its solutions have a blue fluorescence. It does not, like anthracene, yield a compound with picric acid.

Anthracene hexahydride, $C_{14}H_{16}$.

Occurs along with the former; fuses at 63°, and boils at 290°; its physical properties, solubilities, &c. are quite similar to those of the dihydride. A tetrahydride, which was formerly assumed, does not exist.

Monomethylanthracene, $C_{15}H_{12} = C_{14}H_9 \cdot CH_3$.

Discovered in 1874 by Weiler†, and since then often examined, occurs in coal-tar in small quantities ‡. It crystallizes from hot alcohol in thin, very bright, light yellow scales; fuses at 200° (Weiler, Fischer) or 208–210° (Wachendorff and Zincke); sublimes in greenish scales; boils above 360°. Insoluble in water; little soluble in alcohol, ether, glacial acetic acid; easily soluble in chloroform, carbon disulphide, and benzene. Nitric and sulphuric acids dissolve it slowly cold, more quickly when hot. With picric acid it yields a compound similar to that yielded by anthracene. The formula given by Laurent to his "paranaphthene" was also $C_{15}H_{12}$; but he cannot have had a pure compound before him.

Dimethylanthracene, $C_{16}H_{14}$.

Was synthetically prepared by Van Dorp in 1872 §, but not directly proved to exist in coal-tar. It resembles the preceding, and fuses at 224–225°.

Phenanthrene, $C_{14}H_{10}$.

This isomer of anthracene was discovered at the same time by

* Ber. deutsch. chem. Ges. 1868, p. 187.
† Ibid. 1874, p. 1185.
‡ Japp & Schultz, ibid. 1877, p. 1049.
§ Ann. Chem. clxix. p. 207.

Graebe * and by Fittig and Ostermeyer †. It is found in the last fraction of the coal-tar oils, as a constant companion of anthracene, and forms a large portion of the crude anthracene. It is obtained from the raw material by many times repeated crystallization from alcohol, in which it is much more soluble than anthracene, and is also obtained in the factories in the purification of the latter; most easily from crude anthraquinone by extracting it with alcohol and recrystallization. It is best to remove phenols and acridine by treating the product with caustic-soda solution and sulphuric acid. Moreover its lower boiling-point can be utilized for a preliminary separation of it from anthracene; its much lower fusing-point facilitates its identification.

Phenanthrene, when pure, crystallizes from alcohol in colourless scales with a faint blue fluorescence. It fuses at 99–100°, boils at about 340°, and sublimes in scales, less easily than anthracene. It dissolves at 13°·5 in 48 or 50 parts of alcohol (readily when hot); also in ether, benzene, glacial acetic acid, and carbon disulphide. In alcoholic solution it yields with picric acid reddish-yellow needles, fusing at 143–145° and soluble in hot alcohol without decomposition. Nitric acid dissolves it, forming a nitro-compound; sulphuric acid at 100° forms a sulphonic acid. Bechi (*loc. cit.*) gives its solubility as follows:—In 100 parts of

Absolute alcohol, at 16° = 2·62, at 78° = 10·8 parts;
Toluene „ 13°·5 = 33·02, „ 100° in all proportions.

The structural formula of phenanthrene is now generally assumed to be

$$\begin{array}{l} C_6H_4—CH \\ | \qquad\quad \| \\ C_6H_4—CH \end{array}$$

, *i. e.* it is a derivative of diphenyl.

Pseudophenanthrene, $C_{16}H_{12}$.

Fuses at 115°; discovered by Zeidler ‡ in that portion of crude anthracene which is soluble in acetic ether, along with

Synanthrene, $C_{14}H_{10}$,

fusing at 189–195°. Nothing accurate is known of these bodies. The latter is probably identical with methylanthracene.

* Ber. deutsch. chem. Ges. 1873, p. 861.
† Ann. Chem. cxlvi. p. 361.
‡ Chem. Centralbl. 1877, p. 566.

Fluoranthene, $C_{15}H_{10}$.

Syn. idryl. Discovered in 1877 in coal-tar by Fittig and Gebhardt*. It probably stands in the same relation to fluorene ($C_{13}H_{10}$) as phenanthrene ($C_{14}H_{10}$) to diphenyl ($C_{12}H_{10}$). It accompanies pyrene in the highest-boiling fractions of coal-tar, and can be separated from pyrene only by many crystallizations from alcohol, preferably those of its compound with picric acid. It crystallizes from dilute alcohol in broad, shining, large plates; from a concentrated solution, in needles. It fuses at 109°, and afterwards sublimes. It dissolves with difficulty in cold alcohol, readily in ether, chloroform, benzene, carbon disulphide, glacial acetic acid, and boiling alcohol; dissolved in concentrated sulphuric acid by gently heating, it gives it a greenish-blue, at a higher temperature a blue, and ultimately a brown colour. With nitric acid it yields a trinitro-product; with picric acid in alcoholic solution, reddish-yellow needles fusing at 183°, and decomposed on boiling with water or addition of ammonia.

Pyrene, $C_{16}H_{10}$.

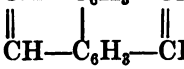
Laurent, in 1837, found it in coal-tar, but probably obtained it only in a very impure state. Graebe, in 1870, prepared it pure†. The fractions boiling above anthracene are extracted with carbon disulphide, the filtrate is evaporated to dryness, the residue dissolved in alcohol, and a precipitate is produced by an alcoholic solution of picric acid, which is several times recrystallized from alcohol, and then decomposed by ammonia. The separated pyrene is recrystallized from alcohol. Colourless tables, fusing at 148°, subliming with difficulty, and boiling a good deal above 360°. Little soluble in cold alcohol, easily in carbon disulphide, ether, benzene, and hot alcohol. Bechi (*loc. cit.*) states that its solubility in 100 parts of

Absolute alcohol, at 16° = 1·37, at 78° = 3·08 parts;
Toluene, „ 18° = 16·54, „ 100° very great.

It yields a nitro-product. Its picrate forms long red needles fusing at 222°, decomposed slowly by boiling water, at once by alkalis. Graebe regards it as phenylene-naphthalene, $C_{10}H_6(C_6H_4)$;

* Ber. deutsch. chem. Ges. 1878, p. 2141; Ann. Chem. cxci. p. 295.
† Ann. Chem. clviii. p. 285.

it may also be represented as a diphenyl derivative n which the two nuclei are once more connected by two C_2H_2 groups,

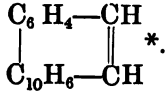


Chrysene, $C_{18}H_{12}$.

Discovered in 1817 by Robiquet and Colin when distilling amber, in 1837 by Laurent in coal-tar; afterwards investigated by many chemists. It is obtained in larger quantity only by distilling pitch as far as coke, mixed with pyrene as a yellow tough mass, sometimes as a dry powder. On extracting this mass with carbon disulphide, it remains behind, and is recrystallized from hot glacial acetic acid or heavy tar-oil. The latter and oil of turpentine are its best solvents; carbon disulphide dissolves only traces. Bechi states that its solubility in 100 parts of

Absolute alcohol, at 16°=0·097, at 78°=0·17 part;
Toluene, „ 18°=0·24, „ 100°=5·39 parts.

It usually forms loose, shining, yellow scales (rhombohedra with straight end face), whose colour, however, is caused by a tenaciously adhering mixture of another substance (chrysogen); in the state of perfect purity it is white. It fuses at 250°, sublimes similarly to anthracene, boils at 436°, but is, at the same time, partly decomposed. With picric acid and binitro-anthraquinone it forms compounds. In concentrated sulphuric acid it dissolves on being heated, with a purple colour; nitric acid yields nitro-products. It is a member of the series increasing by C_4H_2, to which benzene, naphthalene, phenanthrene, chrysene, and picene belong; probably it is



Chrysogen.

Discovered in 1862 by Fritzsche† in coal-tar. It is the substance whose intense orange colour, even in the smallest quantity, imparts its tint to other bodies, *e. g.* to chrysene. Its formula is

* Graebe and Bungener, Ber. d. chem. Ges. 1879, p. 1078; Bamberger and Kranzfeld, ibid. 1885, p. 1931.

† Zeitschr. f. Chem. [2] ii. p. 139.

not yet established; it contains above 94 C per cent. It is isolated by repeated crystallization from light tar-oil and washing with ether and alcohol. It dissolves in 500 parts of boiling or 2500 parts of cold benzene, 2000 of boiling or 10,000 of cold glacial acetic acid. It is best obtained from boiling alcohol, in yellow scales, cohering like sal-ammoniac; the thinnest scales are pink, with gold-green lustre. Even $\frac{1}{3000}$ of it colours naphthalene an intense yellow; but its solutions are quickly bleached in the sun, star-shaped groups of colourless needles being formed. It fuses at 280–290°, being partly decomposed; in concentrated sulphuric acid it dissolves without change.

Retene, $C_{18}H_{18}$.

Discovered in 1837 by Fikentscher and Trommsdorff, in coal-tar by Krauss*, studied especially by Fritzsche†. Shining, unctuous scales, devoid of smell and taste, fusing at 98–99°, solidifying again at 90–95°, boiling at 350° without change, but volatilizing a little even at the ordinary temperature, strongly in the water-bath. Sinks in cold water, but floats on hot. Insoluble in water, little soluble in cold alcohol, readily in hot alcohol, ether, fatty and essential oils. At a red heat it yields much anthracene.

Succisterene

is hardly a distinct chemical compound, but probably a mixture. Pelletier and Walter describe it as devoid of smell and taste, fusing at 160–162° and distilling above 300°, very little soluble in alcohol and ether. Analysis yielded 95·5 C and 5·6 H per cent.

Picene (*Parachrysene*), $C_{22}H_{14}$.

Discovered by Burg‡ in browncoal tar, but very probably present in the heaviest tar-oils; identical with Rasenack's parachrysene§. It is very similar to chrysene, but even less soluble, viz. very little in boiling glacial acetic acid, benzene, and chloroform, best in coal-tar oils; boiling between 150° and 170°. Its fusing-point is higher than that of any other known hydrocarbon, viz. 337–339°,

* Ann. Chem. Pharm. cvi. p. 391.
† Journ. prakt. Chem. lxxv. p. 281.
‡ Ber. deutsch. chem. Ges. 1880, p. 1834.
§ Ibid. 1873, p. 1401; Wagner's Jahresb. 1873, p. 813.

corrected =345°, and it boils at 518–520°. It dissolves in concentrated sulphuric acid, with a green colour.

Precisely the same body was found by Graebe and Walter* in a product obtained by dry distillation of the purification residue of Californian petroleum. They found its formula $=C_{22}H_{14}$, which makes it a member of the series mentioned on p. 134. It fuses at 330–345°, and boils (as determined by Craffts's air-thermometer) at 518–520°. Hence also its boiling-point exceeds that of any other hydrocarbon of known formula.

Benzerythrene, $C_{24}H_{18}$.

Discovered by Berthelot†, prepared in the pure state by Schultz‡ and recognized as triphenylbenzene. Fuses at 307–308°. Small, white, shining, strongly electric scales. Little soluble in alcoholic or even boiling glacial acetic acid, more so in hot benzene; soluble in sulphuric acid, with a green colour.

Bitumens.

Badly characterized hydrocarbons, fusing with great difficulty, assumed to be present in coal-tar pitch. Carnelley§ distinguishes two bitumens:—one boiling at 427–439°, which is readily soluble in benzene and carbon disulphide, moderately in ether; and the other boiling above 439°, hardly soluble in benzene, but more easily in carbon disulphide. The latter softened at 190°, began to fuse at 220°, but was not quite liquid till it reached 330°. Both were black masses with conchoidal fracture. Evidently Carnelley himself does not assume that those two bodies were homogeneous compounds.

Oxygenized Compounds.

Water, H_2O.

Methylic Alcohol, CH_4O.

Syn. wood-spirit, wood-naphtha. Boils at 63°; sp. gr. at 0° 0·818, at 20° 0·798. Occurs in wood-tar, and especially in crude wood-vinegar; not yet proved with certainty to occur in coal-tar.

* Ber. deutsch. chem. Ges. 1881, p. 175.
† Ann. Chim. Phys. [4] ix. p. 458.
‡ Ber. deutsch. chem. Ges. 1878, p. 96.
§ Journ. Chem. Soc. 1880, p. 714.

Ethylic Alcohol, C_2H_6O.

Syn. spirit of wine. Boils at 78°·5; sp. gr. at 0° 0·8095, at 15°·5 0·7939. According to Witt* it constitutes 2 per cent. of crude benzol; Vincent and Delachanal† also found the same; but Krämer‡ doubts the fact. Possibly the difficulty arises from the circumstance that their "crude benzol" had already been treated with sulphuric acid and caustic-soda liquor, in which case it might happen that, from the ethylene dissolved in the tar, sulphovinic acid was formed, and decomposed by the alkaline treatment with formation of alcohol. Watson Smith also explains the formation of alcohol in this way; but he could only find small traces of alcohol in London benzene.

Acetone, $C_3H_6O = CH_3-CO-CH_3$.

Boils at 56°; sp. gr. 0·7921 at 18°. Soluble in water, alcohol, ether, &c., in all proportions. Very inflammable.

Acetic Acid, $C_2H_4O_2$.

Boils at 119°; sp. gr. at 15° 1·057. Extremely important as is its occurrence in wood-tar, it seems to be nearly, if not quite, absent from coal-tar. Vincent and Delachanal (*loc. cit.*) found it on distilling crude benzol with alkali, as a product of the decomposition of methylic cyanide.

Benzoic Acid, $C_7H_6O_2$.

Melting-point 121°·4; boils at 249°·2. Found in the residues from the manufacture of phenol by K. E. Schulze (Ber. d. chem. Ges. 1885, p. 615).

Phenol (*Carbolic Acid*), C_6H_6O.

Syn. phenylic acid, phenylic alcohol. Discovered in 1834 by Runge§, more exactly examined by Laurent, and subsequently by many chemists. It was for a long time confused with Reichenbach's "Creosote" from beechwood-tar, in spite of Runge's and Laurent's protestations, owing to the authority of Reichenbach,

* Chem. Centralbl. 1878, p. 415.
† Compt. Rend. lxxxvi. p. 340.
‡ Chemische Industrie, 1878, p. 126.
§ Poggend. Ann. xxi. p. 69, xxxii. p. 308.

Gmelin, and others; hence "creosote" came to be practically synonymous with "carbolic acid" (acide phénique), till all doubts were cleared up by Gorup-Besanez*. It occurs much more abundantly in coal-tar than in other tars. In the pure state it forms long white needles, fusing at 42°·2 into a clear, colourless liquid, and boiling (under a pressure of 760 mms.) at 184° without decomposition. Ordinary "pure" phenol, which contains traces of cresol or water, fuses at about 35°·5, and boils at 188°. Hence the phenol examined by Adrieenz†, and considered exceptionally pure, which fused at 37°·8, solidified at 34°·3, and boiled at 183°·3–184°·1, was not absolutely pure. Really pure phenol, fusing at 42°, is less deliquescent than that melting at 35°, which contains a little cresol. In damp air phenol absorbs water, and its fusing-point is lowered by the formation of a *hydrate*, C_6H_6O, H_2O, containing 16·07 per cent. of water and fusing at 17°·2‡. It seems to be the same as that obtained by Calvert on exposing a mixture of 4 parts of phenol with 1 part of water to a temperature of 4°, although he states its fusing-point to be 16°, and its formula $2(C_6H_6O)$, H_2O. The hydrate begins to lose water at 100°, and thus gradually arrives at the boiling-point of anhydrous phenol.

In very damp air the hydrate absorbs still more water, and then remains liquid. If to phenol as much water is added as can be mixed with it, the resulting liquid contains about 27 per cent. water, almost exactly corresponding to the hydrate C_6H_6O, $2H_2O$. But on shaking this liquid with 4 vols. of benzene, it gives up the whole of its phenol to the latter, the water being separated (Allen).

The specific gravity of phenol at 18° is 1·065; its expansion for the temperature t at the pressure of 760 millim. is stated by H. Kopp as follows:

$$V_t = 1 + 0{\cdot}0006744t + 0{\cdot}000001721t^2 \quad 0{\cdot}00000000050408t^3.$$

Adrieenz (*loc. cit.*) gives the following table of the volumes of phenol:—

* The history of creosote has been accurately elucidated by Schorlemmer (Journ. Soc. Chem. Ind. 1885, p. 152).

† Ber. deutsch. chem. Ges. 1873, p. 443.

‡ Allen, The Analyst, iii. p. 319.

Temp.	Sp. gr.	Volume.
40°	1·05433	1·01504
50	1·04663	1·02259
60	1·03804	1·03036
70	1·02890	1·04028
80	1·01950	1·04984
90	1·01015	1·05951
100	1·00116	1·06899

In spite of being deliquescent, phenol is not very easily soluble in water, but is so in all proportions in alcohol, ether, benzene, glacial acetic acid, glycerin, &c. The usual statement is that phenol dissolves in 20 parts of water; and some give even a much higher figure. Alexeieff gives the following data:—100 parts of water at 11° dissolve 4·83, at 35° 5·36, at 58° 7·33, at 77° 11·83 parts of phenol; at 84° both liquids mix in all proportions. Conversely 100 parts of phenol at 9° dissolve 23·3, at 32° 26·75, at 53° 31·99, at 71° 40·72 parts of water. On the other hand, Allen states that liquid aqueous carbolic acid dissolves in 11·1 times its volume of cold water, corresponding to pure phenol dissolving in 10·7 times its weight of water or to the aqueous solution containing 8·56 per cent.* According to Hamberg†, pure carbolic acid (fusing-point 40–41°, solidifying-point 39°, boiling-point 180–180°·5) dissolves at 16° or 17° in 15 parts of water, and at 40° in two vols. of liquor ammoniæ of sp. gr. 0·96 (forming a clear liquid which turns milky at 17° or 18°). Other statements, attributing to it a less considerable solubility, must be explained by the presence of cresol, which lowers the solubility. The aqueous solution does not redden litmus; benzene, ether, carbon disulphide, or chloroform abstracts phenol from its aqueous solution. Cold petroleum-spirit dissolves but little of it (compare below).

The smell of carbolic acid is very similar to that of wood-tar creosote (that is, smoky), but (like the taste) it is less pronounced in very pure phenol than in impure; so that in the former case it

* Other observers have found that phenol containing some water is much more soluble in an excess of water than anhydrous phenol; this perhaps explains the difference between Allen's observations and those of other chemists.

† Ber. deutsch. chem. Ges. 1871, p. 751.

can be masked by a few drops of geranium oil, which also keep it always liquid. The taste of phenol is burning and sweet at the same time: it violently acts upon the epidermis, turning it white and hardening it or making it shrink. Hence it must be cautiously handled; rubbing with a fatty oil lessens the pain and the bad consequences of an external contact with it. Internally it acts of course as a poison, both by its corrosive action on the epithelium and by its property of coagulating albumen; it seems to act upon the nervous system by paralyzing the nerve-centres. According to Allen even a momentary contact of strong acid with an extended surface of the lower parts of the body is mostly fatal, but on the arms it acts comparatively little.

The poisonous and coagulating properties of phenol are very specially exhibited by its preventing the development of lower organisms; this has made it one of the most important agents for the prevention of fermentation and putrefaction, for Lister's treatment of wounds, &c.; and its technical application, apart from its employment in the manufacture of a few colouring-matters, of salicylic acid, &c., is exclusively owing to its antiseptic property.

The solutions of phenol in oil do not possess the same disinfecting power as those in water (Koch, Wolffhügel, and Knorre, Journ. Soc. Chem. Ind. 1882, p. 244).

Phenol not quite pure turns red more or less quickly, especially under the influence of air and light. The cause of this is not quite certainly known; perhaps it is owing to the formation of rosolic acid by the influence of traces of mineral acids, in the presence of homologues and of oxygen. Frequently the reddening of phenol is attributed to traces of copper*, or of other metals as well †, which are said to form compounds of a red colour with phenol, but not rosolic acid (Kremel). Rosolic acid is assumed to be the cause, *e.g.* by Yvon ‡; other oxidized compounds by Ebell §.

The following reactions are characteristic for phenol. A drop of a dilute solution of phenol gives with a solution of 1 part of molybdic acid in 10 of concentrated sulphuric acid a yellow-brown

* *E. g.* Sicha, Journ. Soc. Chem. Ind. 1882, p. 397.

† Kremel, Chem. Zeit. 1886, Rep. 14; Meyke, Fischer's Jahresber. 1883, p. 513.

‡ Pharm. Journ. Transact. 1881, p. 1051.

§ Repert. analyt. Chemie, 1884, p. 17.

colour, soon turning purple. Heating to not above 50° assists the reaction. Since many other bodies cause the reduction of molybdic acid, this reaction is interfered with by them.—By addition of ferric chloride (not in excess!) 1 part of phenol in 1000 or at most 1500 (not 3000, as usually stated) can be recognized by a purple colour; but some neutral salts interfere with this, and, on the other hand, other compounds show the same reaction.—Twenty cubic centims. of a solution of 1 part of phenol in 10,000 water, mixed with a very little liquor ammoniæ and then with a little fresh saturated chlorine-water, or, preferably, bromine-water, produce a deep indigo-blue colour. This reaction is very stable, the colour remaining unchanged for days and weeks even in the open air.—On heating phenol solutions with $\frac{1}{3}$ to $\frac{1}{2}$ their bulk of a 10- or 15-per-cent. solution of mercurous nitrate, a pink colour appears, which is strongest 1 or 2 hours afterwards. This reaction is almost as sensitive as the next, and remains for some time.—Even 1 part of phenol in 80,000 water can be discovered by adding fresh bromine-water, a white crystalline precipitate of tribromphenol ($C_6H_3Br_3O$) being formed, but in the case of very dilute solutions not till after some time.

The quantitative estimation of phenol will be described in Chapter IX.

Phenol is the type of a whole class of bodies which stand as it were midway between alcohols and acids. Hence the older and industrially most usual name, "carbolic acid," is hardly used in scientific writings. The phenols form a class by themselves, viz. those aromatic compounds in which the hydrogen atoms of benzene nuclei are replaced by hydroxyl (OH). The hydrogen of the latter is easily replaced by metals or alcoholic radicals; but the other characteristics of a real acid are absent.

Phenol is consequently more soluble even in dilute alkaline solutions than in water, with formation of easily soluble and crystallizable compounds (*e. g.* with potash, soda, or ammonia) called carbolates or phenates (C_6H_5ONa, &c.). These compounds are not very stable; they are not decomposed by dilution with water, but by heating in the dry state, which liberates the phenol. Ether and alcohol dissolve these compounds. Hence the phenols can be separated from the indifferent tar-oils by treatment with an alkali.

Concentrated sulphuric acid also dissolves phenol with formation

of sulphonic acids, and thus removes it from tar-oils, which, however, easily retain a little of the sulphonic acid. Nitric acid yields nitro-products, one of which is technically important, viz. picric acid, $C_6H_2(NO_2)_3OH$. In the presence of bodies which can furnish methane carbon, along with free mineral acids and oxygen, rosolic acid, $C_{19}H_{14}O_3$, is formed. Upon this is based the technical preparation of coralline from phenol, oxalic acid, and sulphuric acid—and perhaps also the reddening of impure phenol, cresol $[C_6H_4(CH_3)(OH)]$ furnishing the methane carbon.

Cresols, $C_7H_8O = C_6H_4(CH_3)(OH)$.

Syn. oxytoluene, cresylic acid.

There are three isomers of this formula; coal-tar seems to contain a mixture of them. The isomers can only be prepared in the pure state synthetically.

Orthocresol (1, 2) fuses at 32° and boils at 188°.

Paracresol (1, 4) forms colourless prisms, fusing at 36° and boiling at 199°. It smells like phenol, and is little soluble in water. Its aqueous solution, like that of metacresol, is coloured blue by ferric chloride.

Metacresol (1, 3) boils at 201°; it is usually obtained as a thick liquid, not solidifying at −80°; but Staedel* has shown that it can be obtained solid on cooling down to −18° and starting the crystallization by adding a crystal of phenol. The crystals melt at +3° or 4°. According to Ihle† and to Tiemann and Schotten‡ very little of it occurs in coal-tar; but it is all the more difficult to understand why coal-tar cresol is always liquid.

Commercial cresylic acid, a mixture of the isomers, is a colourless, refractive liquid, does not solidify at −80°, has a specific gravity of 1·044, is much less soluble in water and alkalis, and boils at a higher temperature than carbolic acid, about 185–203°. It gives the same reaction with ferric chloride as carbolic acid, and is even more strongly acted upon by strong sulphuric and nitric acids. With bromine it gives a tribromo-compound, $C_6HBr_3(CH_3)(OH)$, liquid at ordinary temperatures. Its antiseptic properties are even more strongly marked than those of carbolic acid.

Allen has given the following table on the differences between

* Ber. d. chem. Ges. 1885, p. 3443.

† Journ. prakt. Ch. [2] xiv. p. 442 (1876).

‡ Berichte, 1878, pp. 767, 783.

carbolic acid (Calvert's No. 1) and cresylic acid (prepared from Calvert's No. 5 by fractionating) :—

	Carbolic Acid.	Cresylic Acid.
1. Melting-point	Solid at ordinary temperature; liquefied by addition of water; both absolute and hydrated acid solidified by freezing-mixture.	Liquid at ordinary temperature; neither absolute nor hydrated acid is solidified by freezing-mixture.
2. Boiling-point	182°	198–203°.
3. Solubility of hydrated acid in cold water.	1 vol. in 11	1 vol. in 29.
4. Solubility in strong solution of ammonia (sp. gr. 0·880).	Completely and readily soluble in equal volume; solution not precipitated by addition of less than 1½ volume of water.	Almost insoluble; requires 16 volumes; then forms crystalline scales.
5. Reaction with solution of caustic soda (free from alumina) containing 6 per cent. NaOH.	Completely soluble in equal volume. Addition of the alkali solution, even up to 6 volumes, causes no change.	Insoluble in small proportions. With large excess it disappears and forms crystalline scales.
6. Reaction with solution of caustic soda containing 9 per cent. NaOH.	Completely and readily soluble in equal volume. On addition of any proportion of water up to 7 volumes the liquid remains clear, but is precipitated by 8 measures of water. Soluble in 2 measures of soda, and not precipitated by less excess than 5 or 6 measures.	Soluble in equal volume, but precipitated by adding a few drops of water, the original volume separating when water is added amounting to 1 measure. The solution in soda is re-precipitated when the alkali solution is added to the extent of 3½ measures.
7. Reaction with petroleum-spirit.	Absolute acid is miscible with hot petroleum-spirit in all proportions. Miscible with only ½ vol. of cold petroleum-spirit, precipitated by greater proportion. With 3 vols. of petroleum-spirit, bulk unchanged; upper layer contains carbolic acid, which crystallizes out on sudden cooling by freezing-mixture.	Absolute acid miscible in all proportions. No separation of crystals or liquid produced by suddenly cooling solution in 3 measures of petroleum-spirit.

	Carbolic Acid.	Cresylic Acid.
8. Behaviour with glycerin of sp. gr. 1·258.	Miscible in all proportions. One measure of carbolic acid with an equal volume of glycerin is not precipitated on addition of 3 measures of water. In presence of cresylic acid less dilution is possible, 2 vols. of water being the maximum for a sample containing 25 per cent. cresylic acid.	Miscible in all proportions. One measure of cresylic acid, mixed with 1 measure of glycerin, is completely precipitated by 1 measure of water.

According to this, cresylic acid is less soluble than carbolic acid in water, ammonia, glycerin, and caustic-soda liquor, but more easily in petroleum-spirit. Hence, though the presence of considerable quantities of cresylic acid can be discovered in carbolic acid, the utilization of those reactions for a quantitative estimation of these bodies is out of the question. An approximate estimation of this kind will be described in the 9th Chapter.

Lunge and Zschokke* have made experiments on the lowering of the fusing-points of pure phenol and pure paracresol by one substance being mixed with the other in definite proportions. The results of their observations are given in the following table:—

Phenol.	Paracresol.	Fusing-point.
per cent.	per cent.	°
100	0	+40·5
95	5	27·8
90	10	23·9
85	15	20·3
80	20	16·7
75	25	12·6
70	30	8·6
65	35	4·7
60	40	+ 0·75
55	45	− 2·5
50	50	− 2·5
45	55	− 0·9
40	60	+ 1·2
35	65	3·5
30	70	6·7
25	75	12·4
20	80	16·2
15	85	20·8
10	90	25·9
5	95	28·5
0	100	+32·5

* Chemische Industrie, 1885, p. 6.

Since commercial cresylic acid contains other isomers as well, the foregoing table cannot be directly utilized for analytical purposes.

Xylenols (*Xenols*), $C_8H_{10}O = C_6H_3(CH_3)_2OH$.

Of the six xylenols admitted by theory, four are known. In coal-tar probably several of these occur; it is also probable that the "*phlorol*" from beach-wood tar (boiling at 220°) is such a mixture*. The pure compounds have been obtained synthetically.

Orthoxenol (1, 2, 4) $= C_6H_3(\overset{1}{C}H_3)(\overset{2}{C}H_3)(\overset{4}{O}H)$. Fuses at 62° and boils at 225°. Crystallizes from water in long needles, from dilute alcohol in orthorhombic octahedra; yields a soluble sodium salt in thin needles.

Metaxenol I. (1, 2, 3) $= C_6H_3(\overset{1}{C}H_3)(\overset{2}{O}H)(\overset{3}{C}H_3)$. Long needles or plates, fuses at 74°·5, and boils at 211–212° (Jacobsen), or at 73° and 216° respectively (Fittig and Hoogewerf).

Metaxenol II. (1, 3, 4) $= C_6H_3(\overset{1}{C}H_3)(\overset{3}{C}H_3)(\overset{4}{O}H)$. Colourless, strongly refractive liquid of sp. gr. 1·0362 at 0°, does not easily solidify in the cold, except when brought into contact with a crystal of the same mass (Staedel and Hoeltz, Ber. d. chem. Ges. 1885, p. 2921); the crystals melt at 26° (Jacobsen, ibid. p. 3464). Boils at 211°·5, little soluble in water, miscible with alcohol and ether. Its alcoholic solution is turned green by ferric chloride, its aqueous solution blue, whilst the other xenols do not give any reaction with that salt. Found in blast-furnace tar by Watson Smith (Journ. Chem. Soc. Jan. 1866 and priv. comm.).

Paraxenol (1, 3, 4) $= C_6H_3(\overset{1}{C}H_3)(\overset{3}{O}H)(\overset{4}{C}H_3)$. Colourless crystals, very like metaxenol I., fuses at 74·5–75°, boils at 211·5–213°·5, sp. gr. at 18° 0·9709. Solubility like that of the above.

There are higher phenols known, viz.:—*mesitylol*, C_9H_{11}. OH, boiling at 220°; *pseudocumenol*, C_9H_{11}. OH, boiling at 240°; *thymol*, $C_{10}H_{13}$. OH, boiling at 230°; *carvacrol* (same formula), boiling at 233–235°; but their existence in coal-tar is not proved.

Neither are the oxyphenols proved to occur in coal-tar, whilst in wood-tar they and their ethers are most important, especially *pyro-*

* Marasse, Ann. Chem. Pharm. clii. p. 75.

catechol, $C_6H_4(OH)_2$, *homopyrocatechol*, $C_6H_3(CH_3)(OH)_2$, the methylic ether of the former (*guaiacol*) and that of the latter (*creosol*).

Naphthols, $C_{10}H_8O = C_{10}H_7 . OH$.

Both isomers have been found in the "green-oils" obtained in the manufacture of anthracene by K. E. Schulze (Annal. d. Chem. ccxxvii. p. 143).

α Naphthol forms brilliant needles, belonging to the monoclinic system, smells similar to phenol, and has a burning taste. Sp. gr. 1·224. It melts at 94–96°, and boils at 278–280°. Sparingly soluble in hot water, easily in alcohol, ether, benzene, &c. Volatilizes with steam. A solution of chloride of lime with an aqueous solution of *α* naphthol causes a deep purple coloration and the separation of purple flakes; ferric chloride gives a white turbidity soon passing into purple.

β Naphthol forms monoclinic scales, almost devoid of smell, of a burning taste, sp. gr. 1·217; melts at 122–123°, boils at 294°, volatilizes very little with steam. Solubility like that of *α* naphthol; but chloride of lime causes only a faint yellow coloration, and ferric chloride first a greenish colour, then the separation of permanently white flakes.

Anthrol and Phenanthrol, $C_{14}H_{10}O$,

have been found, although not separated in the pure state, in the oils accompanying anthracene by Noelting (Ber. d. chem. Ges. 1884, p. 386) by treating the portion boiling above 300° with a solution of sodium hydrate.

Rosolic Acid, $C_{19}H_{14}O_3$.

Syn. aurin. Discovered in 1834 by Runge * in coal-tar; afterwards synthetically prepared at the same time by Persoz † and by Kolbe and Schmitt ‡, but in a very impure state, by treating phenol with oxalic acid and sulphuric acid. Since then it has been examined by many prominent chemists; its constitution, and even its formula, was only ultimately recognized in 1878, at the same time by E. and O. Fischer and by Graebe and Caro. The

* Pogg. Ann. xxxi. pp. 65, 512, xxxii. pp. 308, 323.
† French Patent No. 54,910 of 21st July, 1861.
‡ Ann. Chem. Pharm. cxix. pp. 119, 169.

rosolic acid from phenol, which is probably the same as that contained in tar, has now generally received the formula $C_{19}H_{14}O_3$, or, structurally,

$$\begin{matrix} C_6H_4— & C & —C_6H_4OH \\ \llcorner O — & C & —C_6H_4OH \end{matrix}$$

i. e. a derivative of triphenylmethane, in which three hydrogen atoms are replaced by hydroxyl, and from which one molecule of water is abstracted *. Hence it is formed if three phenol remainders can attach themselves to a carbon atom of the fatty series (methane carbon); and it actually forms an inner anhydride of the trioxy-triphenylmethane-carbinol. It is now pretty generally assumed that its formation from phenol, oxalic acid, and sulphuric acid is caused by the liberation, from the oxalic acid, of CO_2, which in the nascent state gives up its oxygen to oxidize 4H of the phenols and attaches the remainders to the vacant bonds of carbon, thus:—

$$3C_6H_6O + CO_2 = C_{19}H_{14}O_3 + 2H_2O.$$

(The accessory reactions which take place in the formation of corallin, *i. e.* the crude product, must be left untouched here. Nencki †, and Watson Smith and Staub ‡ attribute the formation of rosolic acid to the formic acid generated by the action of sulphuric acid upon phenol.)

We have already (p. 140) pointed out that the conditions for the formation of rosolic acid are given when, besides phenol itself, its higher homologues containing the methyl group CH_3 are present, and if at the same time mineral acids can act upon it by separating water; but there must be an oxidizing action as well: thus

$$2C_6H_6O + C_7H_8O + 3O = C_{19}H_{14}O_3 + 3H_2O.$$

Perhaps this explains why the reddening of phenol requires the presence of air, as well as the reddening of impure naphthalene, which in any case contains some unchanged phenol.

In any case it must be assumed that the rosolic acid found by Runge in coal-tar was only formed by acid treatment of the products. (Whether a mineral acid is absolutely necessary or not, is not yet proved.) He obtained it by exhausting the residues from the distillation of phenol by water, dissolving in $\frac{1}{8}$ of their weight

* Graebe and Caro proposed to keep the name *aurin* for this compound, and to apply that of *rosolic acid* to the higher homologue, made from rosaniline; but this has not been generally accepted.

† Ber. 1882, p. 1578.

‡ Journ. Chem. Soc. 1884, p. 301.

of alcohol, and mixing with lime. Thus he obtained a pink solution of calcium rosolate and a brown precipitate of calcium brunolate. From the former rosolic acid is precipitated by acetic acid, and purified by repeated solution in milk of lime and precipitation by acetic acid till no more calcium brunolate separates. Ultimately, by dissolving in alcohol and evaporating, a hard, glassy, orange-coloured mass is obtained, whose valuable dyeing-properties were pointed out very emphatically by Runge, but were first utilized a generation afterwards.

That an oxidation process takes place in this case seems to be proved by the fact that slow heating of the heavy tar-oils with lime in the presence of air much increases the yield of rosolic acid*. Angus Smith went even further, by heating phenol, caustic alkali, and manganese dioxide †.

Brunolic Acid (?).

Runge thus named an acid which he isolated from the brown precipitate filtered from the solution of calcium rosolate. It was an asphalt-like, glassy mass, undoubtedly a mixture of different chemical compounds.

SULPHURETTED COMPOUNDS.

Hydrogen sulphide, H_2S.

Ammonium sulphide, $(NH_4)_2S$.

Ammonium sulphocyanide, $(NH_4)NCS$.

Sulphur dioxide, SO_2.

These must occur in coal-tar, as they are always present in gas-liquor (compare the last Chapter).

Carbon bisulphide, CS_2.

Boiling-point 47°. Sp. gr. 1·272. Was found in crude benzol by Vincent and Delachanal ‡; it had often been assumed to exist in tar, as it is always found in the gas. Watson Smith has found 6 per cent. of CS_2 in the first runnings of rectified benzol from London gas-tar. H. L. Greville prepared it on the large scale from the calcium-sulphide purifiers of gas-works §.

* Tschelnitz, Wiener Akad. Ber. Jan. 1858, xxiii. p. 169.

† Chem. Gaz. 1858, no. 20.

‡ Compt. Rend. lxxxvi. p. 340.

§ Journ. Soc. Chem. Ind. 1883, p. 488.

Carbon oxysulphide, COS,

has not yet been found in tar, but is sure to exist dissolved in it, since all conditions are present for its formation. It is a colourless gas, smelling of carbonic anhydride and a little of hydrogen sulphide, of very faintly acid reaction. It is extremely inflammable, and with sufficient oxygen yields CO_2 and SO_2; with insufficient oxygen, or on cooling, it yields only CO_2 and S: $COS + O = CO_2 + S$.

Thiophen, C_4H_4S,

was discovered by Victor Meyer* in nearly every description of what was then considered "chemically pure benzol" by shaking it up with concentrated sulphuric acid. Colourless liquid, of a faint and not very characteristic smell. Boils at 84°, sp. gr. 1·062 at 18°.

Benzene containing thiophen gives the "indophenin" reaction, that is, a blue colour on treating with isatin and sulphuric acid. Thiophen is more easily soluble in concentrated sulphuric acid than benzene, and can therefore be completely removed from the latter by long-continued agitation with renewed quantities of sulphuric acid.

Thiotolen (*Methylthiophen*), C_5H_6S.

Discovered by V. Meyer and Kreis†. Similar to thioxen; boils at 113°, sp. gr. 1·0194 at 18°.

Thioxen (*Dimethylthiophen*), C_6H_8S.

Discovered by K. E. Schulze‡; prepared in the pure state by Messinger§; boils at 137°. There is hardly any doubt that higher members of the thiophen series occur in coal-tar as well.

Mercaptans,

or similar sulphuretted compounds having a disagreeable smell, are probably present in coal-tar. The alliol of which Mansfield stated the boiling-point to be 70–80°, and of which he obtained 30 to 40 grams from 50 litres of tar, is perhaps a mixture of such compounds, although carbon bisulphide might be thought of as well. Vohl‖ has found, in crude benzene, sulphuretted bodies boiling below 80°.

* Ber. d. chem. Ges. 1883, p. 1471.
† Ibid. 1884, p. 787.
‡ Ibid. 1884, p. 285.
§ Ibid. 1885, p. 563.
‖ Dingler's Journal, clxviii. p. 40.

			Sp. gr.
Methyl mercaptan, $CH_3 . SH$,	boils at	20°	
Methylic sulphide, $(CH_3)_2S$	„	41°	0·845
Ethyl mercaptan, $C_2H_5 . SH$	„	36°	0·831
Ethylic sulphide, $(C_2H_5)_2S$	„	91°	0·852

&c.

Free Sulphur

has been found by Kehlstadt * in the distillates of coal-tar. It is probably formed from SO_2 and H_2S under the action of water.

Nitrogenized Compounds.

A. Basic.

Ammonia, NH_3,

has been already mentioned as ammonium sulphide and sulphocyanide. It occurs also as carbonate, and forms the most important constituent of gas-liquor. A colourless gas, of the well-known pungent smell, sp. gr. 0·5888, condenses at −40° to a liquid, and solidifies at −70°. Its ready solubility in water, the strongly basic properties of this solution, &c. are universally known.

Substituted Ammonias

of the fatty series occur probably in gas-liquor, and consequently in tar. We shall only quote the boiling-points &c. of the lowest members.

Methylamine, $NH_2(CH_3)$, is a gas. 1 vol. water at 12° absorbs 1040 vols. of it. It is inflammable; it smells like fish and ammonia at the same time.

Dimethylamine, $NH(CH_3)_2$, boils at 8–9°; readily soluble in water. Smell strongly ammoniacal.

Trimethylamine, $N(CH_3)_3$, boils at 9°·3; readily soluble in water. Smells of ammonia and herring-brine, in which it occurs abundantly.

Ethylamine, $NH_2(C_2H_5)$, boils at 18°·7; readily soluble.

Diethylamine, $NH(C_2H_5)_2$, boils at 57°·5; readily soluble.

Triethylamine $N(C_2H_5)_3$, boils at 91°; little soluble.

The higher members and the extremely numerous mixed amines cannot be noticed here.

* Ber. deutsch. chem. Ges. 1880, p. 1345.

Cespitine, $C_5H_{13}N$,

is a base of unknown constitution, isomeric with amylamine and boiling at the same temperature (95°). It was discovered by Church and Owen. A colourless oil of strong smell, less disagreeable than that of amylamine; readily soluble in water, but not in concentrated solution of caustic soda. Lighter than water. Church and Owen suppose in it a trivalent radical $(C_5H_{13})'''$. Fritzsche believed he had found it in coal-tar, but Goldschmidt and Constam consider Fritzsche's cespitine to have been their pyridine hydrate (see below).

Aniline, $C_6H_5 . NH_2$.

Syn. phenylamine, amidobenzene, &c. Discovered in 1826 by Unverdorben, (in coal-tar) 1834 by Runge (who called it kyanol). A colourless liquid, very soon turning yellow, then red or brown, of a peculiar faint smell and burning taste. Solidifies at −8° (some say, not even at −20°), and boils at 182°; the vapour burns readily. Sp. gr. at 16° = 1·020. It possesses poisonous properties, especially for smaller animals. Water dissolves about 2 per cent.; and it dissolves some water itself. Readily soluble in alcohol, ether, acetone, carbon bisulphide, hydrocarbons, &c. It dissolves sulphur, phosphorus, camphor, rosin. The aqueous solution has only faintly basic properties, and does not even turn red litmus blue; but at a higher temperature it expels ammonia from its salts, whilst in the cold it is precipitated by ammonia. With chloride of lime it turns purple; with potassium bichromate, blue. Its aqueous solutions precipitate the oxides from the salts of iron, zinc, and aluminium. With the mineral acids it forms salts which are readily soluble in water and alcohol and crystallize well; they are white when quite pure, but redden quickly in the air and assume a faint smell.

Immense as is the importance of the aniline made from coal-tar benzol, its direct occurrence in coal-tar is yet of small moment. Here it is practically only an impurity, from which the hydrocarbons must be freed by acid treatment; neither does it seem feasible to extract at a profit the small quantity present in coal-tar.

Probably the basic body which former inquirers extracted from coal-tar, and which yielded the characteristic reactions of aniline, contained only a small percentage of real aniline.

According to Watson Smith*, aniline occurs in all distillates of coal-tar, principally (as might be presumed from its boiling-point) in the light oils of sp. gr. 0·900 to 1·000.

The *homologues of aniline* (*toluidine* &c.) have not yet been proved to exist in coal-tar, but it is most likely that they exist there.

Pyridine Series.

This series embraces a number of bases of the formula $C_nH_{2n-5}N$, from pyridine to viridine. They are characterized by the "pyridine nucleus," which is quite analogous to the benzene nucleus, but contains N in lieu of one atom of C. They are very stable, even towards oxidizing agents. They occur chiefly in the tar-oils of sp. gr. 0·900 to 0·990.

The pyridine bases found in coal-tar have been re-investigated by A. W. Hofmann (Ber. deutsch. chem. Ges. 1881, p. 1497), and by Goldschmidt and Constam (ibid. 1883, p. 2976). This and the quinoline series are of very great importance, since it has been proved that the natural alkaloids are derivatives of pyridine, and since some compounds, very useful for medical purposes (*e. g.* antipyrine), have been synthetically produced from them.

Pyridine, C_5H_5N.

Discovered by Anderson in bone-tar, by Greville Williams in coal-tar. Häussermann (private communication) found up to 0·1 per cent. in commercial 50 per cent. benzol, and 0·25 per cent. in the toluol made from this. Its synthesis has not yet been achieved with certainty. A colourless, mobile liquid of penetrating smell. Sp. gr. at 0° 0·9858; boils at 116°·7 (Anderson) or 115° (Thenius). Miscible with water in all proportions, and reprecipitated by caustic potash or soda. Turns red litmus blue, gives off white vapours with hydrochloric acid, precipitates cold the salts of zinc, iron, manganese, aluminium. Resists the action of fuming nitric and chromic acids. With the acids it forms stable salts readily soluble in water and alcohol, which can be dried at 100°, and hardly turn brown in the air.

Goldschmidt and Constam found in coal-tar a molecular compound of pyridine and water, C_5H_5N, $3H_2O$, of sp. gr. 1·0219, boiling at 92–93°, and smelling like pyridine.

* Journ. Chem. Soc. 1874, p. 853.

Picoline, C_6H_7N.

Syn. odorine. Isomeric with aniline. Discovered by Unverdorben in bone-oil, by Anderson in coal-tar. A colourless, mobile liquid of penetrating smell. Boils at 135°; sp. gr. at 0° 0·9613 (Anderson), at 22° 0·933 (Thenius). Its solubility, salts, and basic properties resemble those of pyridine. Coal-tar picoline is no doubt *a* picoline, that is orthomethyl-pyridine (Goldschmidt and Constam), but possibly γ pyridine is also present in small quantities.

Lutidines, C_7H_9N.

The only lutidine found in coal-tar by Thenius and by Oechsner de Coninck * is a colourless liquid, miscible with water, boiling at 153·5–154°·5, of spec. grav. 0·9443 at 0°. It is undoubtedly γ ethyl pyridine, as proved by its yielding, on oxidation, isonicotinic acid.

Quite recently, in a hitherto unpublished research, carried out in the author's laboratory, Rosenberg has found in the "vitriol tar" from a German tar-works three other lutidines, viz. the *aa* lutidine, boiling at 142°, the $a\gamma$ lutidine, boiling at 157°, and the $a\beta_1$ lutidine. The latter has not yet been isolated, but it has been recognized with certainty by its oxidation-product, isocinchomeronic acid.

Collidine, $C_8H_{11}N$.

A colourless, aromatically smelling liquid, boiling at 179°, almost insoluble in water; sp. gr. at 0° 0·921.

Parvoline, $C_9H_{13}N$.

This, as well as the three following members, is very little known. Boils at 188°, sp. gr. 0·966.

Coridine, $C_{10}H_{15}N$.

Discovered by Thenius. A colourless liquid of faint smell, like leather; boils at 211°, does not solidify at −17°; sp. gr. at 22° 0·974. Little soluble in water, readily in alcohol, ether, &c. Yields crystalline salts.

Rubidine, $C_{11}H_{17}N$.

Discovered by Thenius. A colourless oil of faint smell, boils at 230°, turns viscid at −17°, insoluble in water, soluble in alcohol,

* Bull. Soc. Chim. xlii. p. 252.

ether, &c. Sp. gr. at 22° 1·017. It precipitates some oxides from their salts. Its salts do not crystallize well, and turn pink in the air; chloride of lime turns it pink; it stains pine wood moistened with hydrochloric acid a red colour.

Viridine, $C_{12}H_{19}N$.

Discovered by Thenius. A yellowish oil, of sweet aromatic smell; boils at 251°, at −17° not yet solid. Does not colour in the air; very little soluble in water. Sp. gr. at 22° 1·024.

Quinoline Series.

Contains a benzene nucleus attached to a pyridine nucleus. It was first investigated by Greville Williams*, and has latterly become of much more importance, since some of its members have been synthetically prepared and have found practical application.

Quinoline or Leucoline, C_9H_7N.

Discovered in 1834 by Runge. It was assumed for a long time that the "leucoline" found in coal-tar was not identical, but only isomeric with "quinoline" obtained from cinchonine; but it was shown by Hoogewerf and van Dorp† that they are identical. It boils at 239–240° and has a specific gravity of 1·081, a penetrating smell, and burning taste. It is little soluble in water, readily in alcohol and ether. Turns resinous on standing in the air; yields many salts.

Isoquinoline, C_9H_7N.

Found by Hoogewerf and van Dorp along with the former; boils at 236–237°; fuses at 18–23°.

Quinaldine, $C_{10}H_9N$.

The first homologue of quinoline, synthetically prepared by Döbner and von Miller‡, and afterwards discovered to be the constant companion of coal-tar quinoline. It boils at 243°, and is evidently not identical with the following, as proved by the boiling-points.

* Chem. Soc. Journ. [2] vol. i. p. 375.
† Ber. d. chem. Ges. 1883, p. 425.
‡ Ibid. 1881, p. 2812.

Iridoline, $C_{10}H_9N$.

Isomeric with quinaldine and with *lepidine* from cinchonine. Boils between 252° and 257°. Yields crystallizable salts with nitric, hydrochloric, and chromic acids, &c.

Cryptidine, $C_{11}H_{11}N$.

Boils at 274°; isomeric with *dispoline* from cinchonine. Can be separated from the preceding only by crystallization of the platinum double salt. Properties unknown.

In the products from cinchonine there occur more bases of this series, up to $C_{16}H_{21}N$; but these have not been found in coal-tar proper. G. C. Robinson and W. L. Goodwin have, however, obtained the following bases from the "vitriol-tar" of Scotch shale-oil * :—

Tetracoline, $C_{12}H_{13}N$,	boiling at	290–295°.
Pentacoline, $C_{13}H_{15}N$,	„	305–310.
Hexacoline, $C_{14}H_{17}N$,	„	325–330.
Heptacoline, $C_{15}H_{19}N$,	„	345–350.
Octacoline, $C_{16}H_{21}N$,	„	360–365.

Probably there are bases of still higher boiling-points present in that tar.

General Process for preparing the Bases from Coal-tar.

A large quantity of tar is agitated with a mixture of one part of sulphuric acid and two parts of water, if necessary, repeatedly. After some rest the clear liquid is drawn off and boiled in an open vessel, or better in a current of steam, till all mechanically dissolved hydrocarbons have been expelled (along with pyrrol, but, according to some, the pyrrol must have been previously destroyed by the acid treatment). The liquid is now passed through linen cloth, caustic-soda solution in excess added to it, and the whole distilled. The aqueous vapour carries away the bases; if the distillate be not concentrated enough, it is saturated with solid caustic potash, avoiding too much heating; and the oily

* Trans. Royal Soc. Edinburgh, xxviii. (1878) p. 561, xxix. (1879) p. 265. These papers not having been published in any other, more widely circulating periodical, are not noticed in any of the abstracts of other learned societies, nor in the "Jahresberichte," and thus have been generally overlooked. The author has received them through the kindness of Mr. W. B. Syme.

mixture of bases, separating at the top, is decanted. If it contains aniline, fuming nitric acid is cautiously added and the mixture gradually heated to boiling, whereby the aniline is destroyed; the other bases remain intact. Water is added, the precipitate filtered off, and the filtrate again saturated with caustic potash. The decanted oil contains much water, which is absorbed by solid caustic soda; this must be done completely, since otherwise the boiling-points of the more volatile bases are much changed; and for this purpose the caustic soda must be several times renewed. The oil is now methodically fractionated, sometimes as many as 20 times, till the boiling-points are constant. The operation is greatly facilitated and less is lost by decomposition when carrying on the distillations in a vacuum.—Greville Williams destroys aniline and its homologues by heating with potassium nitrite and hydrochloric acid, and then proceeds as above.

The following notes on the isolation of the bases contained in coal-tar are due to a private communication from Dr. C. Häussermann to the author. Since there is rarely a sufficiently large quantity of the mixture of pyridine bases at disposal, which would admit of isolating them by a series of fractional distillations, it can be recommended to employ for the preparation of products of constant boiling-points (at least of the lower members of the series) the benzenoid hydrocarbons, isolated by fractional distillation on a manufacturing scale, which are constantly accompanied by those bases. English 50-per-cent. and 90-per-cent. benzol has always been treated at the tar-works with but a small quantity of sulphuric acid, so that it contains both thiophens and bases. Such benzol, after having been fractionated by a Savalle's column into benzene, toluene, and xylene, boiling at a constant temperature, admits the recovery of up to 0·5 per cent. of pure pyridine from toluene, and as much picolene from xylene. If these hydrocarbons are first treated with dilute sulphuric acid, only the bases are extracted, and are at once recovered in the pure state, the fractionation on the large scale having separated the single bases from one another, while thiophen, thiotolen, and thioxen remain behind, and can be extracted by treatment with concentrated sulphuric acid.—Instead of removing aniline from the basic mixture by oxidation, Häussermann prefers doing this in the shape of aniline sulphate, which is much less soluble than the sulphates of the other bases.

Acridine, $C_{13}H_9N$.

Discovered by Graebe and Caro* in crude anthracene; re-investigated by Riedel† and Bernthsen and Bender‡. Obtained by extracting crude anthracene with dilute sulphuric acid, precipitating by potassium chromate, purifying the chromate by recrystallization, precipitating the base by ammonia, and recrystallizing the same from hot water. Or the hydrochlorate is recrystallized and decomposed by ammonia. Acridine crystallizes in orthorhombic prisms, colourless if very small, brown if larger. It fuses at 111°, distils above 360° without change, sublimes at 100°, and is carried over by aqueous vapour. It is sparingly soluble in cold, more so in hot water, readily in ether, alcohol, carbon bisulphide, and hydrocarbons. It possesses a faint alkaline reaction; but even very dilute solutions of its salts cause acute stinging on the skin; its dust in the most minute quantity causes most violent sneezing. (This property of acridine is sometimes very inconvenient to the workmen in subliming crude anthracene, especially in summer-time, when they have to protect the skin of the face by rubbing fat upon it.) Sulphuric acid attacks it only at 200°; hydrochloric acid and caustic potash do not attack it even at 280°; zinc-dust, soda-lime, and many oxidizing agents not at all. Nitric acid forms nitro-compounds. With the acids it forms salts all of yellow colour, easily soluble and crystallizable. Their dilute solutions fluoresce strongly with a blue colour, more concentrated ones green, the very concentrated ones not at all.

B. Not Basic.

Pyrrol, C_4H_5N.

Discovered by Runge, isolated in the pure state by Anderson. Prepared by distilling the oils (p. 155) after saturation with sulphuric acid, and fractionating. A colourless liquid of chloroform-like smell and burning taste; boils at 133°; sp. gr. 1·077. Little soluble in water, insoluble in alkalies, readily soluble in ether and alcohol, slowly in dilute acids. In the air it turns brown, but is again rendered colourless by distillation. It tinges a piece of fir-wood moistened with hydrochloric acid, first pink, then crimson. It is indifferent towards most reagents, but is perhaps very slightly

* Journ. f. prakt. Chem. [2] ii. p. 183; Ber. deutsch. chem. Ges. 1872, p. 15.
† Ber. deutsch. chem. Ges. 1883, p. 1611.
‡ Ibid. p. 1802.

basic. No salts of it are known. With potash it forms a compound not decomposable by heat, but at once by water. The quantity of pyrrol present in coal-tar is extremely small, and it is a difficult matter to extract it.

Cyanogen Compounds.

We have already mentioned ammonium sulphocyanide. According to Vincent and Delachanal * tar contains also *methylic cyanide* (aceto-nitrile), $CH_3—C\equiv N$, which under the action of alkalis takes up the elements of water and yields acetic acid and ammonia. They found it in Paris benzol, together with carbon bisulphide, in that part of benzol which boils below 80°.

Methylic cyanide boils at 77°; sp. gr. 0·835. A colourless liquid of peculiar, not disagreeable smell, miscible with water in all proportions, and burning with a purple-bordered flame.

Similar compounds have been found in light coal-tar oils by Noelting †, who considers them to be either methyl-isocyanide, boiling at 59°·6, or ethyl-isocyanide, boiling at 78°·1, and ascribes to them the poisonous action sometimes noticed with such light oils.

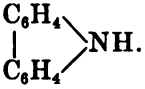
Carbazol, $C_{12}H_9N$.

Syn. imidodiphenyl. Discovered by Graebe and Glaser ‡ in the residue from the purification of anthracene by caustic potash (Chapter VII.), in which a combination of it with potash, decomposable by water, is contained. It is always a considerable constituent of crude anthracene. Its properties are very similar to those of a hydrocarbon; like the hydrocarbons, it forms a compound with picric acid, fusing at 182° in large red prisms, which can be employed for preparing pure carbazol. The latter can also be purified by recrystallizing or subliming. It forms white scales or plates, insoluble in water, sparingly soluble in cold alcohol, ether, benzene, chloroform, more so at a higher temperature: 100 parts of toluene dissolve at 16°·5 0·55, at 100° 5·46 parts; 100 parts absolute alcohol at 14° 0·92, at 78° 3·88 parts. Fusing-point 238°; it sublimes readily, and boils near 355°. It dissolves in pure cold sulphuric acid, the solution having a yellow colour; the most minute traces of nitric acid, chromic acid, chlorine, or

* Compt. Rend. lxxxvi. p. 340.

† Bull. Soc. ind. de Mulhouse, 1884, p. 461.

‡ Ann. Chem. Pharm. clxiii. p. 343, clxx. p. 88.

other oxidizing agents produce an intense green colour. Water precipitates it unchanged from the cold solution in sulphuric acid; by heating, a sulphonic acid is formed. Nitric acid yields nitro-products. Carbazol is not changed by igniting with soda-lime, caustic lime, zinc-dust, &c.; on igniting with potash-lime a portion is decomposed, ammonia being formed. It has no basic properties, and forms no salts with acids, but a compound with acetyl and with potassium, in which the hydrogen of the imido- group is replaced by acetyl or potassium. It is the imido- compound of diphenyl:  .

Phenylnaphthyl-carbazol, $C_{16}H_{11}N$.

Syn. imidophenylnaphthyl. Discovered by Brunck, examined by Graebe and Knecht* (who obtained it also synthetically). Is obtained by subliming the residue from distilling crude anthracene. Intensely yellow, but only by the admixture of some unknown substance; for on being fused with potassium hydrate it turns white. Almost insoluble in cold, very little soluble in boiling benzene or glacial acetic acid, more soluble in hot aniline. Toluene and absolute alcohol, when cold, dissolve next to nothing of it; boiling toluene dissolves 0·39–0·57, alcohol 0·25 per cent. The solutions have an intense blue fluorescence. It fuses at 330°, and has a higher boiling-point than sulphur. Its behaviour to sulphuric acid &c. resembles that of carbazol.

Free Carbon (so-called)

is found in every description of coal-tar, probably owing to coal-dust or coke-dust being mechanically carried out of the retort. It is estimated by treating the tar with indifferent solvents, especially hot benzene, till nothing further is dissolved. The carbon found in German coal-tar by this method varies from 7 to 33 per cent.; tar containing much of it is not very saleable, owing to the difficulty of distilling it down to hard pitch without injuring the stills. It is, however, certain that washing the tar or pitch with benzene &c. does not yield really pure carbon, but only substances similar to anthracite or coke (comp. Behrens, Chapter VI.).

* Ber. deutsch. chem. Ges. 1879, pp. 341, 2241.

CHAPTER IV.

THE APPLICATIONS OF COAL-TAR WITHOUT DISTILLATION.

As we have seen on p. 11, considerable time elapsed after the successful introduction of gas-lighting before means could be devised for disposing of the tar obtained during the manufacture of the gas, or at least before it was regarded as a source of profit. Probably at that time large quantities of the tar were burnt, a process which is not so simple as might appear (see below); probably it was also employed from the first as a cheap paint for wood and metals, although it is but little adapted for that purpose in the raw state. But this could only consume a small portion of the coal-tar obtained, and most of it remained a great nuisance to the gas-manufacturers, who had sometimes to pay considerable sums to get rid of it. This, no doubt, led to the first attempts at utilizing the tar by distillation, which we shall mention in Chapter V.

Before, however, gas-tar was distilled on a manufacturing scale in order to isolate the valuable substances contained in it, of course it had to be employed in other ways, either in the raw state or thickened by evaporation. Even later on the tar could not, and in some places up to this day cannot, be distilled to advantage, principally owing to the cost of carriage; and it was necessary to find other uses for it, in order to get rid of it.

Recently, as we have seen above (p. 5), the great fall in the prices of coal-tar products has led to such a depreciation of coal-tar itself, that the question of disposing of it in other ways than by distillation has become much more urgent than before.

The most obvious plan was to try whether gas-tar could not be employed for *making gas* itself, by passing it through red-hot tubes, or by distilling it and similarly treating the vapour. This was

the intention of the process of Koechlin, Duchatet, and Perpigna*, that of A. Bernard† (who ran the tar upon the coke remaining in the gas-retorts), that of Droinet‡ (who moulded the tar, mixed with ashes, coal-dust, saw-dust, clay, &c., into compact lumps which were heated in ordinary gas-retorts), and that of Isoard§ (whose tar-gas, prepared by superheated steam, contained, according to Monier's analysis, 17·8 per cent. ethylene and 71·9 per cent. "light hydrocarbon," *i. e.* methane—which seems very doubtful). Similar processes are indicated in the English patent of Hengst, Watson, Muschamp, and Wilson (1858), and that of MacCrachen, Newton, Kirkland, and Husson. Still and Lane (Eng. patent, 6 Oct. 1871) mixed tar, together with some vegetable matters, with gas-coal. According to Bunte‖ all these endeavours led to nothing, as those substances which, by decomposing at a high temperature, furnish permanent gases are present in coal-tar in too small a quantity. Nevertheless fresh attempts will be made in this direction now that tar is of so little value. It is true that raw tar seems very badly adapted to gas-making, since the pitch, which forms the greater part of its bulk, is almost devoid of light-giving substances, and since, moreover, the pipes are very easily stopped up in the operation; but it is possible that tar deprived of its pitch, naphthalene, and anthracene, as proposed by G. E. Davis, would be a suitable material for the above purpose. Even this is contested by L. Wright, as we shall see at the close of the next Chapter.

Coal-tar was always extensively employed for the *preservation of building-materials* of all kinds. Stones as well as iron and wood can be preserved much longer, and protected against atmospheric influences, by a coating of coal-tar.

For *stones, brickwork*, &c., especially when exposed to the action of acid vapours, Kuhlmann¶ strongly recommends painting with coal-tar. Long before that, it was usual in chemical works to boil the stones intended for erecting acid-tanks, hydrochloric-acid condensers, chlorine-stills, &c. in gas-tar somewhat boiled down, also to paint the brickwork of the furnaces and any wood

* English Patent of 1854.
† Dingler's Journal, cxlviii. p. 292.
‡ Ibid. cxlviii. p. 295.
§ Ibid. clv. p. 462.
‖ Schilling's Gasbeleuchtung, 3rd ed. p. 231.
¶ Compt. Rend. lvi. pp. 1066, 1146.

or iron work exposed to acid vapours with coal-tar, nay, even to soak the roofing-tiles in the same; and this is done up to this day. It has been noticed at the works that coal-tar not merely renders those objects less liable to be acted upon by damp, acids, &c., but makes the stones much harder and able to resist mechanical wear and tear. Hence the stones intended to be used for acid-cisterns and the like must be completely dressed by the stone-masons before they are put in the tar-pan, because they will not take the chisel after boiling. Fireclay pipes, which in the crude state are not even watertight and are extremely fragile, after boiling in tar become acid-proof, hard, and very little sensitive to changes of temperature. But there is no reason why the employment of coal-tar in this direction should be confined to chemical works. It has been observed that brick-paving lasts very much longer if the bricks have been first soaked in hot tar. This is equally the case with roofing-tiles, and is as good as, though very much cheaper than, glazing them, to make them stand the weather.

On the author's recommendation, a large brickworks has extensively employed hot coal-tar for preparing black roofing-tiles, with complete success. But it must be noticed that a mere dipping in ordinary coal-tar is not sufficient to produce a permanent coating of sufficient strength. The tar should be heated to at least 100° C., and the bricks or tiles &c. should be left in it for some time, till, on breaking a sample, it is found to have rather deeply penetrated into the substance of the brick. The tiles are then left to dry for some time, isolated from one another on convenient frames.

For all these purposes the tar should be deprived of water and of its most volatile oils by evaporation or (much more rationally) by heating in a still; and much the best is the varnish or "refined tar" made from pitch and tar-oil (comp. Chapter VI.).

Tar is also employed for *painting metals*. When laid on hot, as frequently practised by blacksmiths, it produces a shining and lasting black coat. Also cast-iron gas-pipes are mostly protected against rusting by a coat of tar laid on hot. That this is regularly practised in chemical works, has already been said. In such cases it does not matter that such a coat is rather rough and thick. If, however, a thin, equal, shining and lasting coat is required, in the place of raw tar one of the varnishes made from pitch and tar-oils, which are described in Chapter VI., must be employed.

For *preserving wood*, coal-tar was recommended as early as 1799, by Le Bon; but for this purpose it is inferior to wood-tar, which even now is exclusively employed in ship-building. Wood-tar penetrates much more deeply into the pores of wood, covers it with a coherent coat, and the preservative action of its phenols is assisted by its paraffin. The drawbacks of coal-tar are its free carbon and its naphthalene. The former prevents the tar from entering the very finest pores; the latter, volatilizing even at ordinary temperatures, leaves rents in the coat. Some go so far as to say that coal-tar produces interior rotting of the wood; but this has not been positively proved, and the manifold employment of coal-tar in chemical works has never led to such a result. At all events the tar-varnishes are preferable to crude coal-tar for wood-painting also. *Tar-vapours* are said to act even better than tar in preserving the wood; this has been patented by Robbins in the United States, by Paradis in Austria*; the success of this process is, however, more than doubtful, as we shall see when treating of creosote-oil. It is unnecessary to say that coal-tar is in any case very inferior to the "creosote-oils" employed in the proper way for "pickling" timber, as will be described in Chapter VIII.

Rives† recommends as a substitute for wood-tar a mixture of coal-tar, rosin, and lime. A mixture called *sulphur-tar* or *benz-asphalt*, prepared by boiling 2 parts of sulphur with 3 parts of coal-tar, has been strongly recommended as protecting wood, iron, and stone against decay and rust. A similar mixture is the *wood-cement*, employed as a roof-covering (Chapter VI.). A mixture of coal-tar with its own weight of hydraulic lime, Portland cement, &c. is said to liquefy at 70°, and to yield on cooling a soft, pliable varnish, resisting acids and specially adapted for wood under water, water-pipes, and roofing-tiles (Dreyssig, G. P. 10,685). Wildhagen (G. P. of 1885) recommends a mixture of wood-pulp, coal-tar, glue and water, employed in the cold state.

Coal-tar plays an important part in the manufacture of *roofing-felt*, which is extensively employed (more so on the Continent and in the United States than in England) for covering factories, agricultural buildings, &c. The manufacture is very simple, if suitable sheets of millboard or felt be provided. These are either boiled in completely dehydrated tar, or continuously drawn through

* Wagner's Jahresb. 1871, p. 848.

† Dingler's Journal, clvii. p. 317.

hot tar, the excess being squeezed out by rollers, which at the same time causes the tar to penetrate into the interior of the felt, Since the tar in being dehydrated loses some of its valuable oils, this operation should never be performed (as it used to be) in open pans, but in stills heated by steam, so that the naphtha can be condensed. It is cheaper and undoubtedly better to employ "refined tar," *i. e.* a mixture of coal-tar pitch with heavy tar-oil, freed from anthracene and phenol (Chapter VI.). Roofs made with this material must be repeatedly painted with a similar mixture, especially during the first years, and are mostly covered in between with a thin layer of sand; but it has latterly been asserted that the sand covering does much more harm than good, and ought to be omitted, since it makes the paper crack and prevents the tar from soaking into it. On the other hand, roofs will be less fire-proof if not sanded.

Even in 1868, of the 9000 tons of tar produced at the Berlin gas-works, only one sixth part was distilled; five sixths were worked up for roofing-felt. It is different now.

Coal-tar is also used for painting the wooden floors of hospitals, barracks, workmen's dwellings, &c., in order to make them water-tight, and to diminish the danger from germ-infection. One kilog. of coal-tar suffices for a surface of 10 square metres = 107 square feet*.

The *antiseptic* property of coal-tar has for a long time been known and made use of; its action as a paint on wood depends partly upon this. No doubt it results from the fact that tar kills the lower organisms. For this reason it has also been tried against the potato- and grape-disease; but in these cases the cure may be worse than the evil. Vines treated with coal-tar or the heavy tar-oils mostly yield objectionably flavoured grapes, and the wine made therefrom is affected in a similar way†.

E. Koch has patented a mixture of tar with gypsum, sand, lime, silica, or aluminium silicates, as an insecticide manure, and for preserving corn, other seeds, and the roots of vines against the ravages of insects (G. P. 14,616 and 18,637).

* 'Gesundheits-Ingenieur,' 1886, p. 434.

† Cornu (Compt. Rend. Oct. 2, 1882). Watson Smith (priv. comm.) has met with a similar objection in the case of celery grown by the help of manure made from vitriol-tar and lime.

Tar, or mixtures containing it, is frequently used for disinfecting cesspools, sewers, &c. The best-known in England is MacDougal's disinfecting-powder, in Germany Süvern's disinfecting-mixture (100 slaked lime, 15 coal-tar, 15 magnesium chloride). No doubt raw tar is inferior in this respect to the specifically disinfecting-substances it contains, such as phenol and naphthalene.

As one of its direct employments the combustion of coal-tar for the purpose of manufacturing *lampblack* may be classed; but it is not so well adapted for this purpose as the heavy oil distilled from it. According to Newton's patent of 1854, lampblack can be obtained directly by mixing 160 lb. of coal-tar with 200 lb. of slaked lime, adding 18 lb. of alum, and strongly heating the well-kneaded mixture without access of air in fireclay crucibles or iron cylinders, as in preparing bone-charcoal. The product has to be allowed to cool down without access of air, and is at last finely ground. By altering the proportions of tar and lime, all shades between brown and grey can be obtained.

The following exact description of lampblack-making has been given by Nepp*. The tar is employed for heating six steam-boilers, 13 feet long, 2 feet 2 inches in diameter, which jointly supply an eight-horse-power steam-engine. The tar is run into tanks holding two barrels each, one in front of each boiler. Behind the boiler is an oven, in which the gases from the burning tar, which have been partially cooled in their way through the boiler-flues, deposit the soot contained in them upon horizontal and vertical shelves, which divide the oven into several compartments. The lightest particles of soot are deposited in the highest part of the oven; and this does not require to be so often emptied as the middle and lower shelves, which contain most of the lampblack and are emptied directly after the tar has been burnt off. The work lasts six hours and proceeds by turns, three ovens always going together, so that there is always enough steam. In the fireplace a residue of fine coke is found. The ovens are well bound and covered with metal plates. They are 13 feet high; the upper 3 feet project through the roof, so that they are cooled from without. They are accessible from below by an iron door, from above by iron steps. The lampblack is partly left as it is; but most of it is mixed with peat, finely ground under edge-rollers, and sifted before it is

* Chemiker-Zeitung, 1878, p. 222.

sent out. The steam generated in the boilers is employed for driving a peat-mill, manufacturing the casks, &c. The cost of plant is about £400 to £450. The product serves for manufacturing colours, shoe-blacking, black-lead for stoves, &c.

Thenius* describes several lampblack-furnaces of a very simple kind, intended for burning tar-oils, pitch, &c. The furnace for "soot-oil" consists of a metal plate kept red hot from below by a local small fire; it forms the bottom of a brick chamber. Upon this the "soot-oil" constantly drops in a fine stream from a tank, whilst a side door with small holes admits the air necessary for combustion. The smoke enters four brick chambers, communicating with a chimney. When the oil intended for combustion has been used up, the furnace is left standing for a few days, and the four chambers are opened by doors provided for the purpose. The last chamber (next to the chimney) contains the finest lampblack (for lithographers); the third one the next finest (for printers); the second and first contain coarser soot, which is well sifted and sold as common lampblack. The best kind is sometimes further refined (for paper-makers, colour manufacturers, lithographers) by ignition in sheet-iron cases whose covers are luted with clay. They must be heated for some time in a furnace with a good draught, till all empyreumatic oils have been driven off and the soot remains behind without any smell. The cases must be left to cool for several days before opening them, because the soot cools very slowly and would take fire if it were exposed to the air too soon. This is "half-calcined lampblack;" the "thoroughly calcined" article is obtained by igniting the first product once more in fresh cases and treating it as above. 400 lb. of "soot-oil" (*i. e.* heavy coal-tar oil) should yield 20 lb. finest lampblack, 30 lb. seconds, and 20 lb. of the third and fourth qualities. On the metal plates some coke remains, which is knocked off and sold as fuel.

The English plan of calcining soot consists in putting a little of it into a circular iron pan, about 2¼ feet high and 2¼ feet in diameter, lighting it by a red-hot iron, and adding more from time to time as the ignition proceeds. When the pan, being full, leaves off smoking, the cover is put on and its contents are allowed to cool. There is about 25 per cent. loss in this process, which should be conducted in a well-ventilated, closed building.

* Die technische Verwendung des Steinkohlentheers, p. 132.

J. Brönner* burns all waste products of tar-distilling under a specially constructed steam-boiler of somewhat complicated construction, and forces the products of combustion by means of a fan-blast of 7 feet diameter through long flues, provided with ground-in bottom-slides, into a soot-chamber. The slides serve to admit air as well, in order to make different qualities of soot, according to their position, for all technical purposes—such as "fat soot" for oil-cloth manufacturers, and calcined soot of all kinds for patent leather, india-rubber, and printers'-ink manufacturers.

The smoke issuing from the chimney of lampblack chambers is rather offensive; this should be avoided by making the passage of the gases so long that at last all the soot is effectually condensed. In an English works there is a "black-house," 150 feet long, and so divided by partitions as to cause the smoke to traverse a distance of 500 feet; it then passes through a fire in which it is completely consumed.

In lieu of brick chambers the condensation of the soot is said to be sometimes effected in large canvas bags, connected by iron or copper tubes, or at the bottom provided with a copper cap and discharge-valve.

As fresh soot sometimes spontaneously ignites in contact with air, the chamber should be allowed to cool down before collecting the soot.

Thalwitzer (G. P. 9426 and 13,691) prepares lampblack by rotating metal disks, cooled with water, over lamps fed with oil, and removing the soot formed by scrapers.

The colouring-power of soot is all the greater the more it has been purified from tarry matters. Runge† examines it by mixing 1 part of soot with 2 of alcohol and 24 of gum-water (made from 2 parts of gum-arabic), taking up some of the mixture with a dry brush, weighing the brush along with the paint, and painting with it on writing-paper divided into squares. The colouring-properties of the soot correspond to the weight of the paint used and the number of the blackened squares.

Wilhelm and Bohnstadt‡ make *printers' ink* by mixing 100

* Private communication.

† Grundriss der Chemie, 1842, i. p. 65, through Schultz, 'Steinkohlentheer,' 2nd ed. vol. i. p. 91.

‡ G. P. 12,282 and 12,286.

parts of coal-tar with 6 to 15 rosin and 10 paraffin oil, forcing through a sieve, treating with bleaching-powder to destroy the smell, and mixing with 20 to 25 parts of glycerin and 12 to 18 parts of lampblack; for the finer qualities a dark aniline colour is added. Or the tar is first heated with 2½ or 3 per cent. sulphuric acid, neutralized with soda, treated with chlorine as above, mixed with 2½ or 3 parts of lard and 4 or 5 parts of glycerin or 8 to 10 parts of soap. Sometimes they add $\frac{1}{10}$ to $\frac{2}{10}$ per cent. lampblack and log-wood extract with bichromate of potash, alum, or cream of tartar.

For making *patent fuel* (briquettes), coal-tar was formerly used, but it has now been generally replaced by pitch, as will be explained in Chapter VI. In some places it seems to be still used for this purpose.

Coal-tar is also largely employed in the Thomas and Gilchrist *steel-making process*, for manufacturing the "basic" lining of the converters.

Burning Tar as Fuel.

Where all other employments fail to procure a satisfactory outlet for the tar, it must be *burned*; and this is mostly done under the gas-retorts themselves. Its heating-value is, in this case, estimated at once and a half, or even twice that of coke, but this is not borne out by L. T. Wright's experiments (see below). This employment of tar has always been the only practicable one where the distance of the gas-works from tar-distilleries was too great and other uses of tar were too scanty; and during the last great fall of prices the burning of tar as fuel for the retorts has come to the fore again, even in some of the manufacturing centres, where such a process a few years ago would have been thought a ridiculous waste. We must therefore treat this question somewhat at length.

The simplest way of burning tar is by mixing some of it with coke. W. Bäcker (Journ. f. Gasbel. vol. xxix. p. 338) runs tar into the fireplace, about 16 inches below the surface of the coke, and finds that he can thus burn about one pound of tar to four pounds of coke. This is also the plan most usually adopted at English gas-works; but it appears that much less tar is burned here in proportion to the coke. Mr. Trewby states the quantity of tar used at the Beckton works = 5 gall. per ton of coke (Journ. Soc. Chem.

Ind. 1886, p. 563). Mr. Wright (*ibid.*) also considers this to be the best way of burning the tar.

We shall describe some of the most suitable arrangements for burning tar, which equally apply to any liquid or easily liquefiable products of the distillation of tar for which no other outlet can be found (as is occasionally the case with some descriptions of "heavy" or "dead" oil), also to petroleum-residues and the like. We, therefore take our descriptions partly from such places where as yet no tar, but petroleum-residues are burned, as they may be useful for tar as well.

That this subject has recently become of greater importance than previously is best shown by the large number of new patents taken out during the last few years; but we shall more particularly enter upon the description of apparatus seen working on the spot by competent observers.

So long ago as 1862* patents were taken out in the United States by Bidley, by Shaw, and by Linton, for the use of liquid fuel; in 1864 an apparatus, by Richardson, was tried at Woolwich. Aydon and Shpakovsky, in 1865, devised arrangements for injecting the fuel as a spray, the former using steam, the latter a blast of air. Watson Smith used steam to inject creosote-oil for boiler fires about 1867. In 1867, at the request of Napoleon III., H. St. Claire Deville constructed an apparatus, which, however, proved a failure on being put to a practical test in Russia. Audouin, in 1869, invented a more suitable burner. Other more successful burners, which are now being used in Southern Russia, date from 1870 and later.

The simple plan of dropping tar into a hot fireplace is unsatisfactory; the combustion is very incomplete, and the consequence is that clouds of dense black smoke are sent forth (such as are seen hanging over the primitive Tatar distilleries at Baku), along with a very disagreeable smell of partially-burnt tar or petroleum. Hence special means must be employed to prevent these drawbacks. We shall enumerate, in the following, only the more important of the very many different descriptions of apparatus invented for this purpose.

An arrangement for burning tar, which answers its purpose fairly well, is shown in fig. 23: *a* is an iron tank for tar (creosote-oil, &c.), which runs in from a tap *b*, best constructed as an auto-

* Redwood, Journ. Soc. Chem. Ind. 1885, p. 78.

matically-acting ballcock, so that the level shall remain always the same, and the tar run off in a uniform stream through the pipe and out of the tap *c*, in an open jet (so that any choking-up can at once be observed) into the funnel *d*, and from this into a horizontal iron tube *g*, which ends inside the fireplace. In the centre of the tar-pipe is a steam-pipe *f*, which first passes as a worm, *e*, through the tar-tank *a*, and keeps it always warm. A cock, *f*, permits the regulation of the steam-jet, which, as it issues in the

Fig. 23.

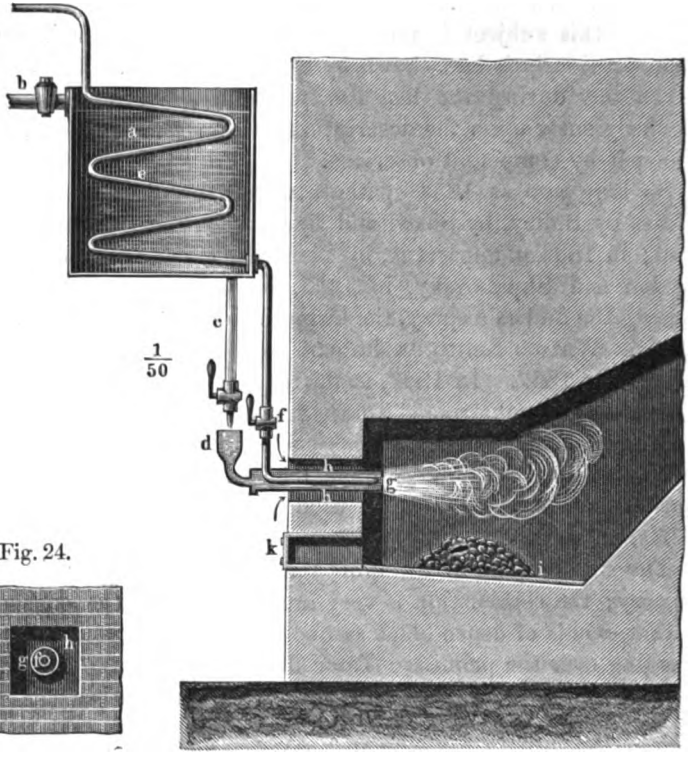
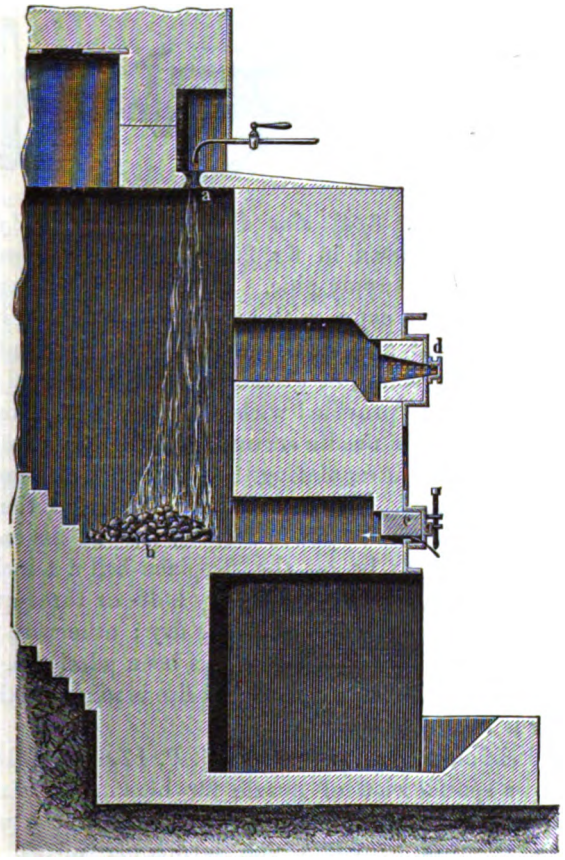


Fig. 24.

centre of the extremity of the tar-tube, converts the tar into a fine spray, and at the same time, acting as an injector, carries in through the open space, *h*, which surmounts the pipe *g*, the air necessary for combustion. Thus the tar is brought into very intimate contact with air, and is almost instantaneously burned; a little of it falls down upon the plate *i*, where it burns into coke, which is removed from time to time through *k*.

Fig. 25 shows a contrivance for burning the tar without a steam-jet, by Liegel*, specially intended for heating gas-retorts by tar. The tar drops through an opening, *a*, 1¼ inch wide, upon a plate, *b*, 5 feet 3 inches below, which reaches through the front wall and is

Fig. 25.

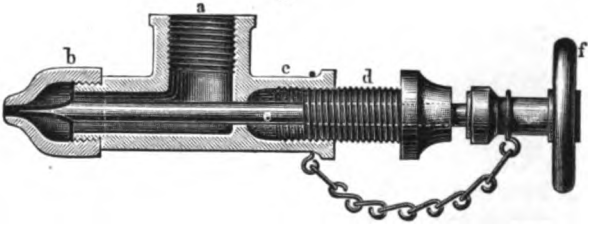


shut off by the door *c*. The latter consists of a slide, moving air-tight on its bed by means of a screw. The air for combustion enters below the slide, and first meets a bed of red-hot tar-coke, collecting on *b*, which it burns into light-grey ashes. The tar is partly burned by the radiated heat of the fireplace; but most of it falls on to the tar-coke burning below, is spread out, and meets

* From Schilling's 'Gasbeleuchtung,' 3rd ed. p. 325.

the air coming in from the door-slide. The small door, *c*, is opened every half-hour for loosening the coke and getting out the ashes. Another door, *d*, with a peep-hole, is placed higher up, and is likewise to be closed air-tight.

Fig. 26.



Schilling (ibid. p. 324) also figures a special "squirting-cock" for the tar, shown in fig. 26. The vertical branch *a* is screwed upon the tar-supply pipe. The end turned towards the furnace is closed by a cap *b* with an opening about $\frac{1}{16}$ inch wide. The other horizontal end, *c*, is provided with a gland through which passes a long screw, *d*, which carries a horizontal needle, *e*. The outer end of *e* is provided with a small wheel, *f*, and is fixed by a small chain. The needle serves for partly or entirely closing the opening (that is, for regulating the jet of tar), also for cleaning it out in case of need. The apparatus is fixed in the furnace-front, so that a slide can be put in front of it. In the case of gas-retorts there ought to be on the fireplace-bed a 4-inch layer of red-hot coke, which is broken up every half- or three-quarters of an hour. This bed ought always to be dry; otherwise too much tar has been run in, or too little air has been admitted. For the purpose of making a start, a small wood-fire is made on the hearth, and the tar is run in at once.

H. T. Litchfield and D. Renshaw (G. P. 17,659, of 1881) have constructed a special kind of nozzle for blowing in a mixture of the combustible liquid with air and steam, in such a way that a converging whirl is caused which intimately mixes the liquid with the air.

Another mixing-apparatus, evidently intended more for petroleum, has been patented by the Boston Petroleum Heating Company (G. P. 21,648, of 1882).

O. D. Orvis* (G. P. 28,017; in England patented as a commu-

* This and a number of other apparatus are described and figured in Dingler's Journal, vol. cclviii. p. 418, and in Wagner-Fischer's 'Jahresbericht d. chem. Technologie' for 1885, pp. 1313-1318.

nication to A. T. Boult, No. 5357, 1883) patents an apparatus, the essential novelty of which is a retort fixed to the inner end of the inlet pipe, in which any less volatile portion of the oil blown in may collect, and may be vaporized by the fire; also a horizontal nozzle through which the mixed stream of steam, hydrocarbon, and air may issue in a sheet-like form.

R. B. Avery (B. P. 5795, of 1883) fits the oil-supply pipe with a series of perforated diaphragms of gradually decreasing mesh, in order to "atomize" the oil before it enters the steam-pipe.

J. H. Selwyn (B. P. 2160, 1884) burns liquid hydrocarbons in conjunction with water-gas or steam in presence of a substance containing both carbon and iron, preferably employing plumbago, in a furnace specially described.

J. Leede and G. H. Ouray (B. P. 1864, 1884, a communication to W. P. Thompson) mix the liquid hydrocarbons with earthy matter, and describe special apparatus for feeding, igniting, and consuming that kind of artificial fuel.

J. D. Bodwell (B. P. 7615, 1885) employs a closed chamber fitted with shelves, sloping downwards from the sides; the oil or tar falls from shelf to shelf, burning during its passage (comp. Nobel's shelf-burner, later on).

H. de Bray and C. D. Rosetti (B. P. 12,990, 1885, a communication to J. Imray) fix to the crown of the fire-flue of an ordinary Cornish boiler a retort, into which oil or tar is admitted; a pipe leads the oil or gases to a receptacle on the fire-bars, to which a supply of air under pressure is also admitted.

A somewhat similar apparatus has been patented by P. Tarbutt (B. P. 5599, 1886).

J. Buffett (G. P. 30,995, 1884) uses the steam first for heating up the oil, before it serves for converting it into a spray.

E. C. Burgess (G. P. 29,614, 1884) avoids the use of a steam-boiler by generating the steam, required for producing the spray from liquid water, by means of a worm and retort fixed within the fire-box.

J. B. Archer (B. P. 6347, 1886) patents an apparatus for firing steam-boilers by means of liquid hydrocarbons which are not "atomized," but are previously gasified.

William de St. Martin (G. P. 36,134) decomposes mineral oils along with steam in a red-hot retort, and mixes the resulting gases by means of an Archimedian screw previous to burning them.

Descriptions of the burning of petroleum-residues at Baku (where they practically are the only accessible fuel) have been given by Boverton Redwood (Journ. Soc. Chem. Ind. 1885, p. 78) and by C. Engler (Dingler's Journal, cclx. p. 440, 1886).

According to Engler, these residues, called "Massud" by the Tatar workmen and "Astatki" by the Russians, form 55 or 60 per cent. of the crude petroleum. Some of it is used up for making lubricating-oils; but much more is burned, partly at the works, to supply the heat for distilling and for raising steam, partly as fuel for steamships and locomotive engines, even at a great distance, on the Caspian, the Black Sea, the Volga, on the Transcaucasian and Transcaspian railways, and so forth.

The heating value is nearly twice that of coal; with burners of the best construction one pound of massud will raise 12 pounds, or with care 14 or 15 pounds, of steam. The distillation of 100 parts crude oil for kerosene consumes three or four parts of massud.

The burners for the residues, called "forsunka," have been principally introduced and improved by O. K. Lenz at Baku. They have very varying forms, but always work so that the oil is atomized by steam previously to burning. The atomizing by compressed air has not answered (compare, however, Nobel's shelf-burner as described below). Even with steam enough air enters to produce complete combustion, and a temperature beyond the fusing-point of wrought iron. Therefore the boiler-plates, heating-tubes, &c. must be protected against the direct action of the forsunka flame.

A very simple forsunka is shown in figs. 27 to 30. The 1-inch iron steam-pipe D is flattened at its end to a slot of $\frac{1}{25}$ or $\frac{1}{50}$ inch width, through which the steam issues. The residues are conveyed by the pipe N; the thick oil spreads over the cup fixed over the steam-nozzle, runs down over the slit, and is converted by the steam into a fine spray. The different nozzles, shown in figs. 27, 28, and 29, serve to produce a more pointed, or a broader, or a medium flame.

The Brandt forsunka (fig. 31) somewhat resembles the spray-producer, or "squirting-cock" (fig. 26, p. 172). The residues, arriving at N, and the steam, from D, are separately carried forward in the tubes *b* and *m*, passing through the brass casting *a*. The massud issues through an annular slit, regulated by the cone *f* by means of the handle *h* and spindle *g*; the steam issues by an outer

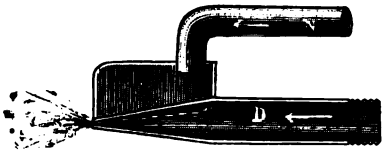


Fig. 27.

Fig. 28.

Fig. 29.

Fig. 30.

Fig. 31.

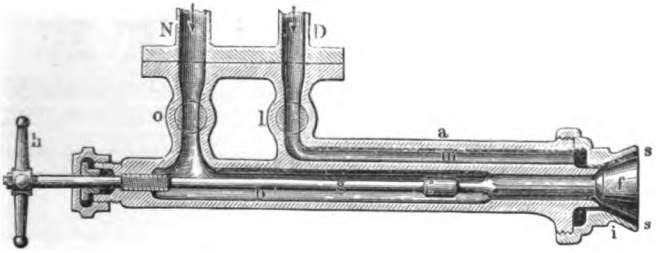


Fig. 32.

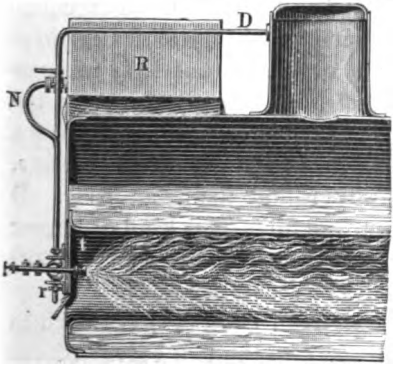
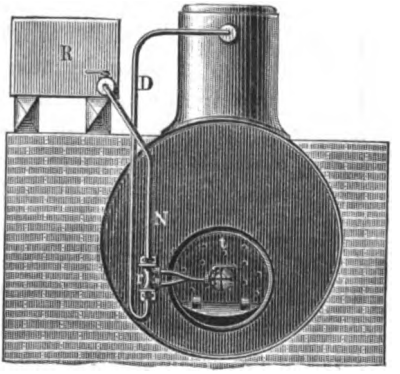


Fig. 33.

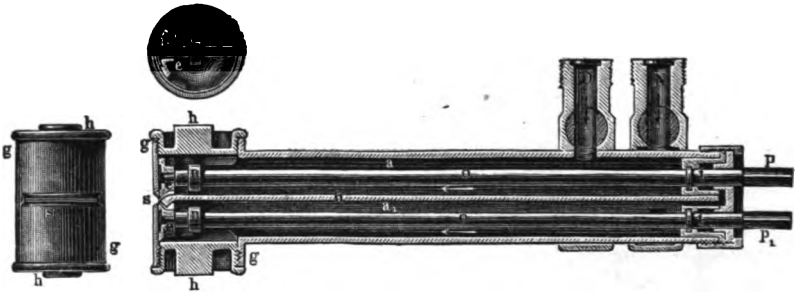


annular slit, concentric with the former. Both are mixed between the cone and the nozzle *i*, and issue at *s s* as a spray which is lighted. The taps *o* and *l* are left open, the cone *f* serving to regulate the process.

Figures 32 and 33 show the application of such a burner to an ordinary Cornish boiler. The residue runs from the tank R through the pipe N into the burner; the steam comes from the dome D. At *r* the whole burner can be turned round in a horizontal plane, so that on turning it 90 degrees it is clear of the door *t*. In this position it is lighted, in order to prevent explosions, and is then turned back. The necessary air enters through the holes in the door *t*, and through a larger opening provided with a regulating valve.

The Lenz forsunka is shown in figs. 34, 35, 36. The double brass-

Fig. 36. Fig. 35. Fig. 34.



tube $a\,a_1$ (fig. 34) ends in the cylindrical mixing-chamber *g*, closed at top and bottom by screw-lids *h h*; the movable rods *o o*, with the key-ends *p* and p_1, turn in bearings at *t* and *n*, and end in excentric pins (fig. 35). The latter work in semicylindrical slides *e*, which are moved up or down by turning *p* or p_1, so that they more or less approach the midfeather *b*, and thus exactly regulate the supply of residues and of steam. The oil is converted into a spray, and issues as a sheet of flame through the horizontal slit *s*, which runs rather less than halfway round the chamber *g*. D and N are taps for shutting off steam and oil. This kind of burner consumes about 3 to 3½ kilog. residues, of specific gravity 0·910 and 140° inflaming-point, per horse-power and per hour.

Sandgreen's burner (also used by Nobel Brothers) is shown in fig. 37. N and D carry oil and steam into the two halves of the

Fig. 37.

chamber A B, separated by the partition *f*. The supply of oil is regulated by adjusting the mouth-plate *k* by means of the lever *h l*, the supply of steam by the mouth-plate k_1 set once for all. The cone *m* permits occasionally cleaning out the compartment A by steam issuing through *g*.

A different description of burner must be used for locomotive and other tubular boilers, where the flame must be spread out. A Lenz burner for this purpose is shown in figs. 38, 39, 40, 41.

Fig. 38.

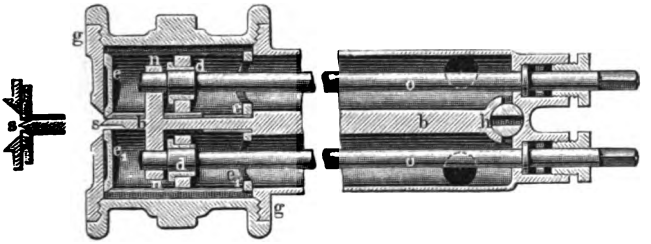


Fig. 39.

Fig. 40.

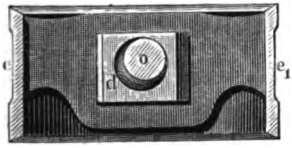
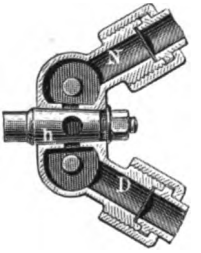


Fig. 41.



It is very similar to the other Lenz burner, figs. 34–36, but the slit *s* runs round the whole chamber *g*, except where it is joined to the burner, so that the spray issues in an annular form.

Hence the slides *e* and e_1 must also be cylindrical, and must move up or down the chamber *g* like pistons. The movement takes place by means of the rods *o*, running in bearings *n*, fixed to the partition *b*. When the excentric rings *d*, attached to *o* (fig. 40), are turned, the cylindrical slides *e* or e_1 are raised or lowered, and thus admit more or less steam or oil through the slit *s*. Fig. 41 is a vertical section through the supply-pipes, D, for steam, and N, for naphtha, &c. The tap *h* allows of sending steam into the oil-chamber for the purpose of cleaning it out. Fig. 39 shows a somewhat altered shape of the partition and of the burner mouthpiece.

Figs. 42 and 43 show a Brandt forsunka, as adapted to loco-

Fig. 42.

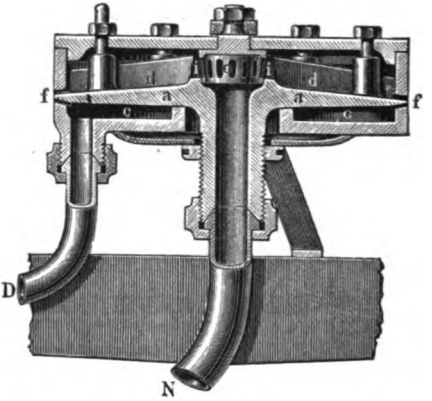
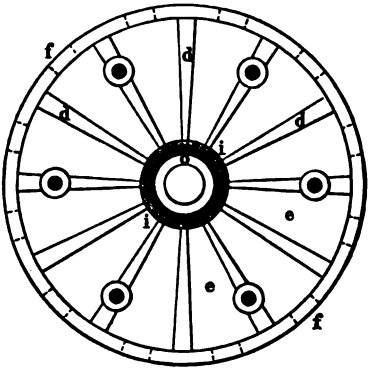


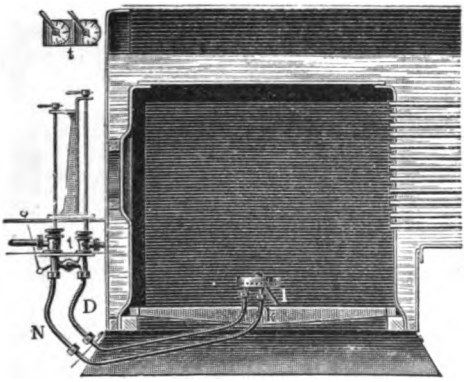
Fig. 43.



motive boilers. The mixing-chamber is divided into two compartments by the horizontal disk *a*. Steam enters into the lower, smaller compartment through D; naphtha &c. into the upper, larger compartment through N. By slightly turning the cap *o*, the slits *i i* are more or less opened, and the supply of residues (naphtha, tar) can be thus exactly regulated. The latter issue radially between the ledges *d* through the sectors *e* and the slits *f*, and are atomized by the steam issuing below.

Fig. 44 shows the same burner *l*, fixed in a locomotive fire-box,

Fig. 44.

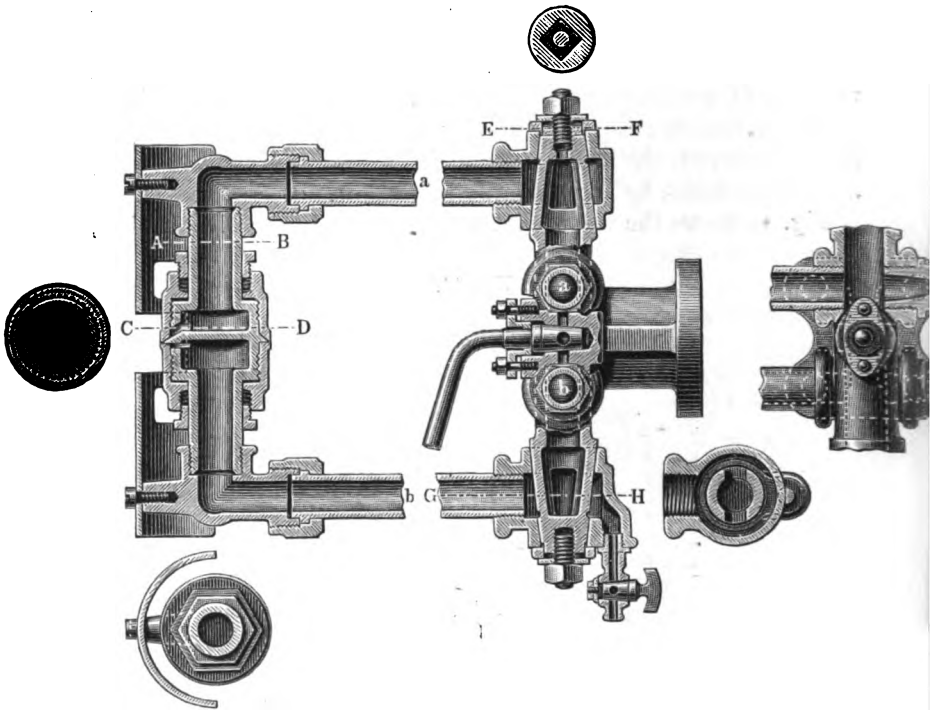


in the centre of the grate *k*. The consumption of naphtha for the transit of a train of twenty loaded trucks, according to Brandt, is about 10 kilog. per kilometre (say 33 lb. per English mile).

Engler praises as advantages of forsunka-firing:—high heating-power, small space for fuel, small volume of the burner, easy working, and, from his own observation, absolute freedom from black smoke in the case of factory chimneys. The locomotive fires are not quite exempt from smoke and smell, but more so than our own, worked with coal. Mr. Redwood, in travelling on those lines, noticed no smoke, but occasionally a disagreeable smell of imperfectly burned petroleum.

The following astatki burners are mentioned in Redwood's description (*loc. cit.*). In Kaufman's burner (fig. 45), which has been adopted by the Russian Government for use in torpedo-boats, the oil enters at *a*, the steam at *b*; they meet at C D, where, by

Fig. 45.

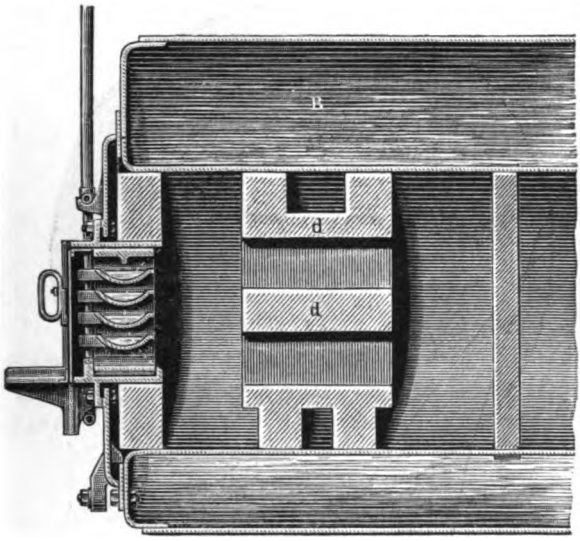


means of two screws, a fissure is opened through which they escape, a spray being produced. The intensely hot pointed flame makes it necessary to employ screens of fireclay in front of the boiler-plate. The roar of the blast is rather objectionable in this apparatus; but, nevertheless, more than a hundred steamers on the Caspian and Volga are fitted with it. There are, of course, no firemen or coal-trimmers, but a single attendant whose duty it is to consult the pressure-gauge from time to time, and to regulate the supply of steam and astatki accordingly. In thus raising steam it is, of course, necessary for a start to take a supply of steam for the blast from a small auxiliary boiler, or to raise steam by an ordinary fire of wood or coal.

In consequence of the objections attaching to the steam-spraying method of burning astatki, Messrs. Nobel have patented an appa-

ratus free from those objections. This apparatus, as shown in figs. 46, 47, and 48 (fig. 46, a vertical section; fig. 48, a sectional

Fig. 46.



plan; and fig. 47, a view of the boiler in front: more details of the plant are given by Redwood, *loc. cit.*), essentially consists of a series of troughs so arranged at the mouth of the furnace that the burning astatki flows by successive stages from the highest to the lowest. Air passes in between the troughs and through the four openings, *c*; the direction of the flame is given by the firebrick walls, *d d*. With this apparatus, 14½ lb. of water can be vaporized by the combustion of 1 lb. of astatki, against only 12 lb. by the "spray" method.

Most remarkable results have been obtained with Nobel's trough-burner for metallurgical purposes. It reduces wrought iron to a state of fusion; and horseshoes, spanners, toothed wheels, and other articles of soft iron can be thus easily and cheaply produced by casting in moulds, without any heating of the air-supply. With this, no doubt, much higher temperatures might be commanded; but the difficulty of finding sufficiently fireproof materials for the furnace stands in the way of making

Fig. 47.

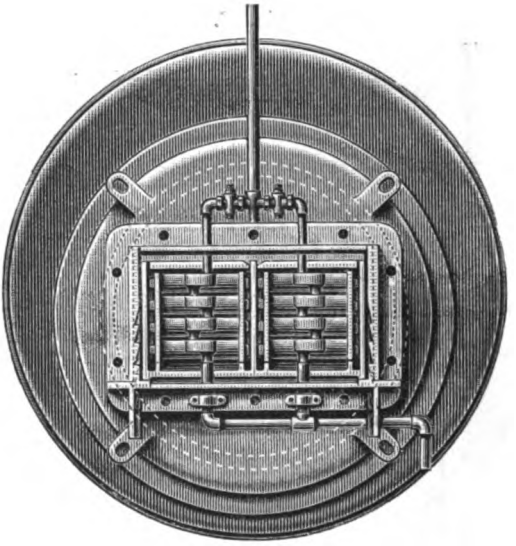
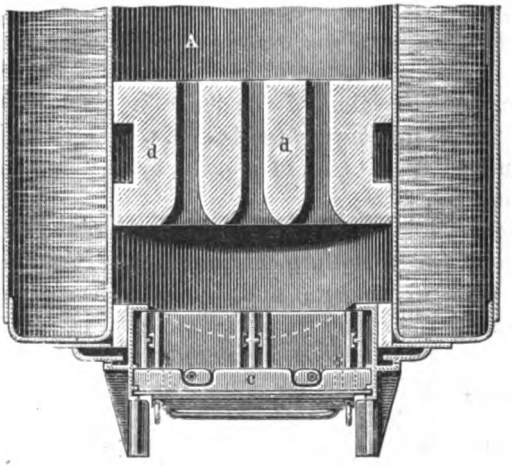
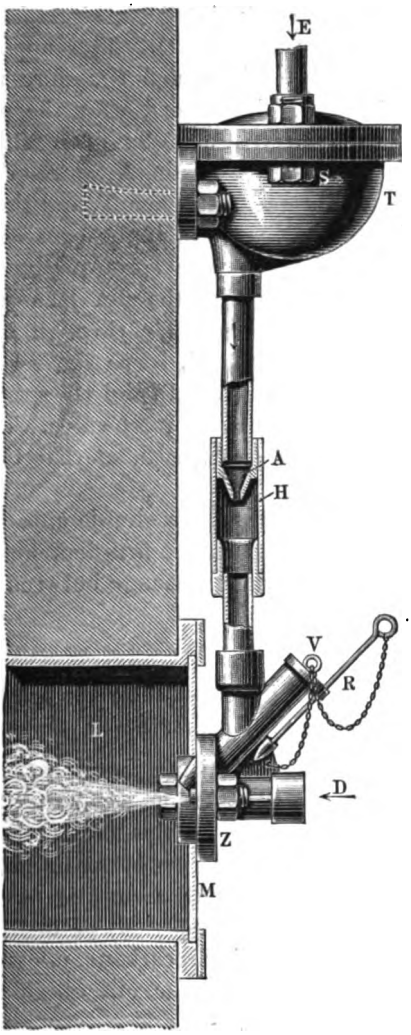


Fig. 48.



experiments in this direction. The freedom of this fuel from phosphorus and sulphur is a great advantage in metallurgical operations. The price of astatki in 1884 was 2*s*. 6*d*. per ton at Baku, or about 8*s*. per ton at Tsaritsin on the Volga; it is largely used in Moscow, and goes as far as Stockholm and Teheran.

Fig. 49.



So far as the use of this fuel for steamships is concerned, the economy of space for storage, and the saving of labour and time in placing it on board ship, must be taken into consideration. At the present price of coal-tar it would perhaps pay to use it for other purposes besides heating gas-retorts, in the same way as astatki, wherever every great heat or where economy of storage are the first considerations.

In conclusion, we mention *Körting's steam-jet spray-producer* (Dingler's Journal, vol. cclx. p. 411). This apparatus, shown in fig. 49, is made entirely of iron, and therefore very substantial and very cheap (£3). It is claimed that the peculiar kind of steam-supply prevents any trace of tar from falling down. The supply of tar is regulated by a nozzle, A, more or less bored out; it is not easily stopped up, as a strainer, T, and sieve, S, retain the impurities. It is also easily accessible for occasional cleaning by moving up the thimble, H. The spray-producer itself can be cleaned any moment by means of the pin R, after lifting up the cover, V. The steam-jet draws air through the box, L, with very great energy; the slides, M, serve for regulating the air-supply. The steam enters through D, and the speed of combustion is regulated by means of the steam inlet-valve. The tar-cistern is placed on the top of the retort-furnace, so that the tar is always heated and thin.

W. Horn (G. P. 36,403) patents a simple apparatus for burning tar &c., which can be hung from the fire-door hinges, and is thus easily put in or taken out when a change between liquid and solid fuel is required.

The Relative Calorific Effects of Coal-tar (with and without Steam) and Coke, for Retort-firing.

At the meeting of the Gas Institute, London (Journ. Gas Lighting, June 29th, 1886, pp. 1242–1244), a paper of peculiar interest at the present time was read on this subject by F. G. Dexter. To obtain the relative calorific values of tar and coke, Mr. Dexter classified the constituents of tar according to their respective boiling-points under the different periods of distillation, and took the average formulæ of the hydrocarbons under these heads as representing the constitution of the oils obtained. The results appear in the following table :—

Constituents.	Average Formula.	Weight, per cent.	Boiling-points.	Proportionate Weight of Constituents.		Calorific Value.	
				Carbon.	Hydrogen.	Carbon Units.	Hydrogen Units.
First runnings	$C_5 H_{10}$	3·0	up to 110°	0·025714	0·004286	200	148
Light oil	$C_{18}H_{14}$	7·0	110° to 210°	0·061091	0·008910	474	307
Middle oils	$C_{12}H_{20}$	27·0	210° to 240°	0·237073	0·032927	1842	1145
Heavy oils	$C_{14}H_{16}$	7·0	240° to 270° and upwards	0·063913	0·006087	497	210
Pitch (56 per cent.), composed of:—							
Oils	$C_{16}H_{10}$	17·5	360° and upwards	0·166336	0·008663	1292	298
Carbon	C	27·5	.....	0·275000	.....	2137	
Gases and water	.....	11·0					
				0·829127	0·060873	6442	2108
			Total.....	0·89		8550	

Coke, when drawn from the retort and slaked, contains fully 25 per cent. of water, besides the ash and sulphur. Ignoring the impurities, and deducting 25 per cent. for water from the value of fired coke, $0{\cdot}75 \times 7000 = 5250$ units per pound of coke are obtained, or, in other words, a relative heating-value for coke and tar of 5 : 8.

By calculating the useful temperatures obtainable from both materials, Dexter arrives at a ratio between tar and coke $=2:1$; but the elements of this calculation are not quite certain, and we would sooner rest on the conclusion taken from practice that the above really represents the respective heating-values of tar and coke.

The practical heating-value of tar is due chiefly to its form and the ease with which it is manipulated. It can be introduced in a small constant quantity, and in a condition much more favourable for intimate mixture with the supply of air than is possible with coke, and consequently the excess of air supplied may be much less. The intermittent cooling produced by fresh charges of coke is also avoided, and thus a much higher heating effect is necessarily produced. The use of steam with tar should be avoided if possible, as it tends to reduce the temperature in the furnace.

This subject is further illustrated by a paper on "The Utilization of Residual Products in Gas-Works" (see Journ. Gas Lighting, 1886, p. 1247) by Mr. J. T. Lewis. The author, in referring to the value of tar, shows that in 1883 the price varied from 1*s.* 8*d.* to 3*s.* 4*d.* per ton of coal carbonized, whereas at the present moment tar is only worth from 4*d.* to 7*d.* The following is the value of tar to tar-distillers, taking the prices of the different products at the present market-value. The statements emanate from two sources, one distiller carrying his process further than the other.

Products from one Still of 8 *tons of Tar.*

	£	s.	d.
Naphtha, 60 gallons, at 9*d.* per gallon	2	5	0
Light oil, 60 „ at 3*d.* „	0	15	0
Creosote, 500 „ at ¾*d.* „	1	11	3
Crude anthracene, 1 cwt.	1	11	8
Pitch, 5 tons, at 15*s.* per ton.....	3	15	0
Wages on the above..... £2 0 0			
Coals 0 6 0			
	2	6	0
Wear and tear, rent, &c., not known			
	£7	11	11

Giving the value of 1 ton as nearly 19*s.*

Products from 1 *ton of Tar.*

	£	s.	d.
Benzene (50/90), 5 gallons, at 1*s.* 5*d.* per gallon	0	7	1
Naphtha ..... 2 „ at 9*d.* „	0	1	6
Carbolic acid ... 5 „ at 1*s.* 8*d.* „	0	8	4
Creosote-oil ..... 50 „ at ¾*d.* „	0	3	1½
Crude anthracene, 30 lbs., at 35 per cent.	0	8	0
Naphthalene ..... 2 cwt., at 3*s.*	0	6	0
Pitch ..... 11 cwt., at 9*d.*	0	8	3
	2	2	3½
Sulphuric acid, caustic soda, slack, and labour for working	0	10	6
Wear and tear, rent, &c., not known			
	£1	11	9½

It is thus seen that tar is not at the present time very valuable to tar-distillers. In cases where the annual quantity of coal carbonized is below 30,000 tons, the distillation is said to be unremunerative. In considering the utilization of tar for fuel, the author gives the following particulars, illustrating the varying values of coke and tar in different localities :—

	s.	d.
(1) Cost of coke for one furnace per 12 hours...	7	4
Cost of coke and tar for ditto	5	2
Saving.....	2	2

Thus showing a saving of 4*s.* 4*d.* for each furnace per 24 hours.

	s.	d.
(2) Coke saved in 24 hours, 1 ton.....	16	8
Tar used, 90 gallons, at 1½*d.* per gallon.....	3	9

Thus showing a saving of 12*s.* 11*d.* per 24 hours. Value of tar as fuel up to 2*d.* per gallon.

	s.	d.
(3) Coke saved, 13 cwt., at 4*d.*, in 24 hours.....	4	4
Tar used, 68 gallons, at 10*s.* per ton	3	5

Thus showing a saving of 11*d.* for each furnace per 24 hours. Tar value, 12*s.* 9*d.* per ton.

When coke is selling at 5*s.* per ton, and tar at 7*s.*, the one can be sold as profitably as the other; but in the majority of cases it will pay better to sell coke than tar.

Much less favourable as regards the value of tar are the statements of L. T. Wright (Journ. Soc. Chem. Ind. 1886, p. 561), according to whom the proportion of steam raised in a Galloway boiler by coke (from Silkstone coal) and by coal-tar was only as 1 : 1·13; in firing gas-retorts the proportion was 1 : 1·17 when atomizing the tar by steam, or 1 : 1·24 by gravitation feeding.

CHAPTER V.

THE FIRST DISTILLATION OF COAL-TAR.

Historical Notes.

It has been mentioned more than once in the preceding chapters that the utilization of tar by distillation is a comparatively new industry; but it had long been known that useful products could be obtained by that operation. In this respect a patent awarded to Henry Haskins, August 7th, 1746 (*i. e.* half a century before the first introduction of gas-lighting), is so remarkable that I quote it verbatim, as follows:—

"New method of extracting a spirit or oil out of tar, and by the same process produce the finest of pitch.

"First, take any quantity of tar you please, so as not to more than half fill your still, which must be thoroughly cleaned from all manner of impurities, and more particularly from water; for if any quantity of that should be left in it, it will be found to be exceeding troublesome and considerably hinder the operation.

"The tar may be cleansed either by boiling or straining, or by settling in tubs, or any other convenient vessel; then commit it to a double-necked pelican-headed still, made either of glass, iron, or copper, with capacious receivers, and well luted, under which raise a fire of the first degree for six hours, by which time the particles will be thoroughly comminuted; then raise your fire to the second degree for as many hours more, and then to the third degree for three hours more, in which time you will find first a pale acid phlegm to come off into the receiver, which must be changed, when a fetid volatile oil or spirit rises; lastly will come over a black glutinous oil, which keep for use.

"If you would have a more volatile or light oil, which may be

more proper for many uses in physic, it may be done by many repeated rectifications to what degree you choose.

"Lastly, the caput mortuum, which is what remains in the still after the distillation is finished, will be found the finest and best of pitch, which I am well assured of, not only from my own judgment, but by the experience and testimony of many who have used it."

It is quite possible that in this patent wood-tar is meant, which at that time was much better known than coal-tar; but the principles of the distillation of the latter appear quite clearly in that old patent.

We have seen (on p. 11) that Accum, in 1815, was the first to boil down coal-tar in closed vessels (stills), and thus to obtain a volatile oil which could be employed as a cheap substitute for spirits of turpentine.

According to Dr. Longstaffe*, the first coal-tar distillery was erected by himself and Dr. Dalston, near Leith, in 1822; the spirits went to Mr. Mackintosh for waterproofing, and the residue was consumed for the purpose of making lampblack.

Roscoe† mentions that, about the year 1834, at the time when Mitscherlich had converted benzene (from benzoic acid) into nitrobenzene, the distillation of coal-tar was carried out on a large scale in the neighbourhood of Manchester; the naphtha obtained was employed for the purpose of dissolving the residual pitch, and thus getting black varnish. Attempts were made to supplant the naphtha made from wood-tar, which at that time was much used in the hat-factories at Gorton, near Manchester, for the preparation of "lacquer," by coal-tar naphtha. The substitute, however, did not answer, as the impure naphtha left on evaporation so unpleasant a smell that the workmen refused to employ it. It was also known, about the year 1838, that wood-naphtha contained oxygen, whilst that from coal-tar did not; and hence Mr. John Dale attempted to convert the latter into the former, or into some similar substance. When trying, for his purpose, a mixture of sulphuric acid and potassium nitrate, he obtained a liquid possessing the smell of bitter-almond oil, the properties of which he did not further investigate. This

* Proc. Soc. Chem. Ind. 1881, p. 13.

† Discourse at the Royal Institution, April 16th, 1886, p. 4.

was, however, done in 1842 by Mr. John Leigh, who exhibited considerable quantities of benzene, nitrobenzene, and dinitrobenzene to the Chemical Section of the British Association, meeting that year in Manchester. His communication is, however, so printed in the Report that it is not possible, from the description, to identify the bodies in question; and hence Leigh's merits in that respect were completely overlooked until quite recently.

The further steps in distilling coal-tar and utilizing the products therefrom, made by Bethell, Brönner, and Mansfield, have already been mentioned (p. 11), and from that time dates the establishment of tar-distilling on a really large scale.

Carriage and Storage of Coal-tar.

Very different descriptions of vessels are used for carrying the tar from the gas-works to the distilleries, according to the circumstances of the case. In England water carriage is preferred whenever it is practicable, the canal-boats being constructed as floating tanks, with a cabin for the crew, which serves also as an air-space for augmenting the carrying-power. Such boats hold as much as 10,000 gallons or about 50 tons of tar. On the continent this is rarely possible; there the tar is usually carried by railway, in cylindrical or angular iron tanks fixed on a platform running on wheels. If these tanks are made of pretty strong iron, they can be steamed out whenever the tar has become too thick, which may happen in winter. Angular (box-shaped) receivers are more easily got at and cleaned inside; they hold about 10 tons, a truck with two cylinders about 9 tons of tar.

Tar-barges or tank-wagons ought to be air-tight, so as to obviate the escape of effluvia (principally sulphide of ammonium) during the transit. While pumping, the cover should only be opened just sufficient for the pipe to pass in.

In Paris (and elsewhere) tar is carried in iron or wooden casks resting on axles and drawn by horses, or, wherever possible, laid on railway-trucks. In Lancashire * it is usual to employ wooden barrels (preferably of ash-wood), holding from 250 to 300 gallons, resting by means of concave wooden bearers upon two-wheeled carts. The middle bearer rests just over the axle; and the barrel

* Watson Smith.

can be tipped behind, two iron adjustments attached to the back bearer preventing it from slipping down. There is a running-off cock of 2- or 2½-inch bore, and a charging-hole 4 or 5 inches square and closed by a wooden plug. Long barrels are said to be pulled more easily than those more bellied. A barrel costs about £3, the cart belonging to it £14.

From the canal-boats or trucks the tar is frequently pumped by steam-pumps into iron *store-tanks*, situated high enough for the tar, after the water has separated, to be run into the stills by natural fall. In Paris the draw-off cocks of the four cylindrical iron store-tanks, which rest on high pillars, unite into a common main, which descends to the ground, runs underneath along the whole set of tar-stills, and gives off an upright supply-pipe with slide-valve for each still, by which these can be filled as required, by means of the hydrostatic pressure, from the store-cylinders. In other cases the tar, especially when it arrives in casks, is emptied into larger store-cisterns sunk in the ground, and pumped from these either into the above-mentioned high tanks, or directly into the stills.

Such underground tar-wells (as well as those for ammoniacal liquor) are frequently of very large dimensions*, as tar-distillers are generally bound by contract to rid the gas-works of their tar and ammoniacal liquor, which in the event of stoppages of business, accidents to the plant, &c., might cause them considerable embarrassment. On the other hand, if there is large storage room, a good stock may be collected in winter, when the gas-works are busiest, so that even in summer the stills can be regularly employed (Watson Smith).

Underground wells are not often made of iron, this being too costly and subject to corrosion. Usually they are made of brickwork set in cement, of a circular shape, secured underneath and round the sides by clay puddle. First the necessary excavation is made; then a good puddle is laid down on the bottom, completely levelled, and a double floor of bricks in cement laid on, the joints crossing each other. Now the sides are raised, likewise in double courses and hence 9 inches thick, leaving between the brickwork and the soil (in case of need kept back by wooden stays) a space of 8 or 12 inches, which is filled in with puddled clay. The best method of proceeding is to complete each time a ring of about

* Watson Smith mentions some of 60 feet diameter.

four feet high, puddle behind it, and continue the walling. It is best not to work too fast, so that the brickwork may have time to settle; cracks once formed can hardly ever be repaired (Watson Smith).

The tar-wells are often tightly covered with planks, to keep off the rain &c. At the place where the carts are tipped there is a strainer with many ½-inch holes and with sides and back, so that any bits of wood which might choke the pumps are kept back (Watson Smith). Or else all the carts discharge their contents into a large spout, provided with outlets for each cistern (if there are several).

The tight covering-in of the tar-cisterns also avoids any nuisance from offensive gases whilst running-in the tar. For this purpose the air driven out by the tar is made to pass through a box containing hydrated oxide of iron, which absorbs any sulphide of hydrogen escaping.

The *pumping* of tar is nearly always done by ordinary donkey-pumps. Raising by compressed air, which is so much employed in this industry, does not answer so well for the tar itself. The suction-pipe is perforated at the bottom with a number of holes, or is surrounded by a strainer, in order to prevent choking up by chips of wood or the like.

The pumping of tar can also be effected by closing the upper reservoir air-tight and producing in the same a vacuum by means of a Körting's steam-jet air-aspirator, or the like; the tar will then be aspirated from the lower reservoir and rise into the higher one.

Distillation by Steam.

The manufacture of coal-tar products begins by fractionally distilling the tar, mostly by a naked fire, but in some places or for special purposes by means of *steam*. The latter plan is now very little used at large works—except in Scotland, where it appears to be general. Its advantage is only apparent where the tar has merely to be dehydrated and deprived of its most volatile constituents in order to employ the remainder (95 per cent.) for painting, for impregnating stones or roofing-tiles, or for the manufacture of roofing-felt (comp. p. 163). In such cases much trouble and danger of fire is avoided by substituting steam for a naked fire. The steam can be applied indirectly, as "dry steam,"

by surrounding the still with a jacket, or by means of a coil in which the steam circulates inside the vessel and issues again to the outside. In the outlet it is expedient to fix an apparatus for automatically discharging the condensed water, without allowing any steam to escape, of which apparatus many kinds are now made. The still may be of almost any shape; perhaps the best is an upright cylinder. The escaping vapours are condensed in a leaden or iron worm and separate in the receiver into ammonia-water and light oil, which is mostly sent to the larger tar-distillers for rectification.

It is more usual to employ "wet" steam, directly blown into the still, *e. g.* by means of a coil of pipes lying on the bottom and perforated with many holes. According to Ure such stills hold from 800 to 1500 gallons, and the distillation is carried on till the specific gravity of the distillate has reached 0·910. According to Mills* the stills hold from 500 to 4000 gallons, and are horizontal cylinders; the steam brings over about 10 per cent. at most of light naphtha (sp. gr. 0·78–0·83) and some ammoniacal liquor. The residue is run into cisterns, where, on its settling, tar and water separate. The "boiled tar" is now ready for the above-mentioned purposes, or can be run while hot into other stills for distilling by naked fire, which is the usual course followed in Scotland. But this process is not advantageous, because there remains very much water with the tar, which can only be separated from it by being allowed to settle for some time; hence if a naked fire is to be used, it is best to do so from the first.

Sometimes the "boiled tar" resulting from the first distillation is not discharged into a tank, but is pumped out through a pipe from the steam-still into a second still, heated by an ordinary fire, so as to avoid any exposure of the hot tar to the air or evolution of disagreeable fumes.

The condensation of the escaping steam and naphtha-vapour, owing to the large quantity of the former, is rather more troublesome than when the distillation is effected with "dry" steam or with a fire. There is much more cooling needed, *i. e.* longer worms and more cooling-water. The condensing-mixture of naphtha and water divides at once into these two constituents, which can be kept apart by overflow vessels, as will be mentioned hereafter in describing the rectification by steam of the lightest oils (Chapter XI.).

* 'Destructive Distillation,' p. 23.

The usual yield of naphtha by this plan is 2 to 6 per cent. from ordinary tar, or 10 to 20 per cent. from cannel-coal tar. The longer the operation is continued, the more, but the heavier, naphtha is obtained.

The *naphtha* obtained by steam distillation is of course richer in volatile constituents than that obtained by direct distillation of tar. But it is far from containing only such constituents as boil at and below the temperature of the blown-in steam (rarely above 150°); a quantity of much higher-boiling substances are carried along, as shown by the following analyses*:—

	I.	II.	III.	
Oils up to 100°	20·9	14·2	29·3	per cent.
„ 130°	5·9	13·2	8·0	„
„ 160°	8·7	19·6	15·2	„
„ 202°	16·0	16·6	23·9	„
Oils boiling above 202° (by difference) . .	48·5	36·4	29·6	„

		sp. gr.
I.	Naphtha from the tar of the Hamburg gas-works,	0·964
II.	„ „ „ Berlin English „	0·947
III.	„ „ „ „ Corporation „	0·932

Hence this product is nothing like so valuable as the "first runnings" of distillation over a naked fire, and is more similar to the "light oil" of that operation.

In Scotland†, instead of distilling by steam, sometimes a fifth of its bulk of water is added to the tar and the whole distilled by a direct fire. Less, but better, naphtha than by steam distillation is said to be thus obtained. This process comes to the same thing as distilling by steam of ordinary atmospheric pressure, but does not seem worthy of recommendation, as the danger of boiling-over is very great.

Distillation by Fire.

The more usual way of distilling tar, by a direct fire, has for its primary object the removal of the non-volatile or too-little volatile constituents, which form the greater portion of tar, in the shape

* From Kerl-Stohmann's 'Chemie,' 3rd ed. vi. p. 1172.

† Ronald and Richardson, 'Chemical Technology,' vol. i. p. 733; Mills, *loc. cit.* p. 23.

of pitch, and to effect a preliminary fractionation of the distillates, which are then worked up singly. It is evident that this can be done only by a direct fire, since the boiling-point of the most valuable product from tar, anthracene, coincides with that of mercury (360°).

Dehydration of the Tar.

It is the first condition of a quiet regular distillation that the tar should be freed as much as possible from the ammoniacal liquor which is always mixed with it to a certain extent, and whose presence is a disturbing element in the distillation. So long as water and tar-oils boil at the same time, there is always a tendency of the liquid to "bump," or even to be jerked over explosively. This can be overcome by very cautious, slow firing; but shortening this stage of the work is decidedly desirable, although it is hardly possible to do without it altogether. Hence *previous dehydration* of the tar is decidedly advisable whenever it can be done without too much trouble.

If the tar be sufficiently fluid, mere prolonged rest will separate a large portion of the ammoniacal water from it; for as the water is only mechanically suspended in the tar and is of less specific gravity, it will rise to the surface, whence it can be drawn or ladled off. In many places nothing else is done for this purpose but storing the tar in several large cisterns, which are best placed at such an elevation that the tar can be run from them straight into the stills. Whilst one of these cisterns is being filled by pumping in fresh tar, the others are allowed to rest; and from that which has stood longest the now somewhat dehydrated tar is drawn off*. At some of the best works a closed steam-coil is laid in the cisterns, by means of which the tar can be heated at will, in order to make it more fluid and to separate the water better. In summer there is no occasion for this; but in the colder seasons the tar is heated to 20° or 21°, sometimes up to 40°. There is hardly any perceptible loss of benzol at this temperature, as there is a layer of water on the top of the tar.

A more complete separation of tar and ammonia is aimed at by the invention of J. and R. Dempster (B. P. 3245, 1882). To the

* According to Watson Smith, at small works tar and gas-liquor are allowed to settle in the same tank; the tar is drawn off by a tap in the bottom, the ammoniacal liquor by one placed higher up, into their respective stills.

opening, out of which the liquor or tar passes, a suitably-shaped box is fixed, having a vertical pipe screwed therein, with an overflow-cup on the top, which can be raised and lowered by means of a screw to suit the height of liquor in the vessel, so that it can flow over the edge of the cup down the screwed pipe into the box, and out at the outlet.

In Germany a number of gas-works (18 in 1886) employ Kunath's separator, as supplied by the Berlin-Anhalt Engineering Company (G. P. 15,255) (figs. 50, 51, 52). The principle of this

Fig. 50.

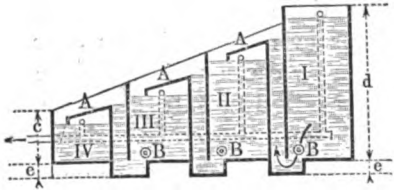


Fig. 51.

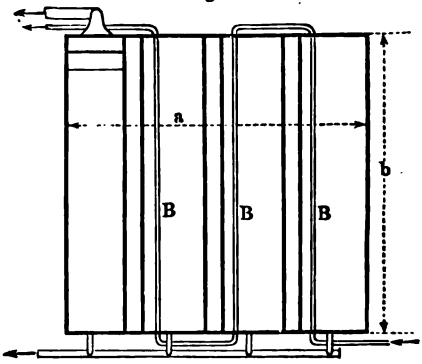


Fig. 52.

apparatus is to spread the tar on broad overflow-spouts. The tar, slightly heated by means of the steam-pipes B B, on running over the spouts A A separates from the water. This separation is further promoted in the vessels I, II, III, IV by the water overflowing near the top by the lateral pipes, whilst the tar passes on at the bottom in the direction indicated in No. 1 by the arrow, and is carried on to the top of the next-following vessel. The outlet of the water in vessel I is situated so much higher than the spout A in the vessel II, that the difference in height corresponds to the difference in specific gravity between tar and water. There are 7 sizes of this apparatus, for separating from 1000 up to 8000 litres (225 to 1777 gallons) per 12 hours.

According to Girard and Delaire*, the dehydration of tar is effected by heating to from 80° to 90° in large boilers, by means of a steam-coil or jacket, or by a direct fire. The volatilizing oils are condensed. After from 20 to 30 hours the separation of tar and

* Dérivés de la Houille, p. 7.

water is sufficiently complete, so that the water collecting at the bottom (?) of the boiler can be drawn off by a cock. The tar is now charged hot into the stills. If this description were correct, it would be precisely similar to the process described on p. 194; only it is called a dehydration instead of a distillation as we have (assuredly more correctly) called it. But we have already stated that a division of the distilling-process into two phases, by steam and by direct fire, whether it be theoretically correct or not, does not seem to have stood the test of practical experience, for none of the largest works proceed in this manner. Girard and Delaire's description is evidently at fault in that it makes the water collect *below* the tar, which is impossible in the case of coal-tar. The same error is committed by Bolley*, undoubtedly from a confusion between coal-tar and browncoal-tar &c. In consequence of a similar inconceivable confusion, C. Vincent† states the specific gravity of *coal-tar* as 0·85 or 0·94!

Perhaps the most rational method of dehydrating the tar is the following, practised at one of the largest and best German tar-distilleries as the commencement of the distillation-process itself. The tar is pumped as it is into the (very large) stills, until it begins to run out of a small overflow-cock placed just below the upper dome of the still, when the pumping ceases and the firing is started. Before the tar arrives at the boiling-point, it has, of course, turned quite thin, and most of the water has collected on its surface. But as by the heating the bulk of the liquid is increased and its level rises above that of the overflow-cock, the watery portion can be drawn off by opening that cock from time to time. Even if a little tar should come along with the water, no harm is done. Whatever vapours are given off during this heating must pass on to the condensing-apparatus, and are thus utilized.

A special dehydrating still, "alambic à circulation," has been patented by Th. Foucault (supplied by L. Poillon, 158 Boulevard Montparnasse, Paris). Figs. 53 and 54 show its construction. It is a rectangular box, A, heated only at one side, and divided into two unequal parts by a perpendicular partition C, also by a slanting plate B. The cover is formed by an inverted pyramid K, in which circulates cold water, introduced through I, and running

* Chemische Technologie der Gespinnstfasern, p. 27.

† Payen's 'Précis de Chemie industrielle,' 1878, ii. p. 944.

Fig. 53.

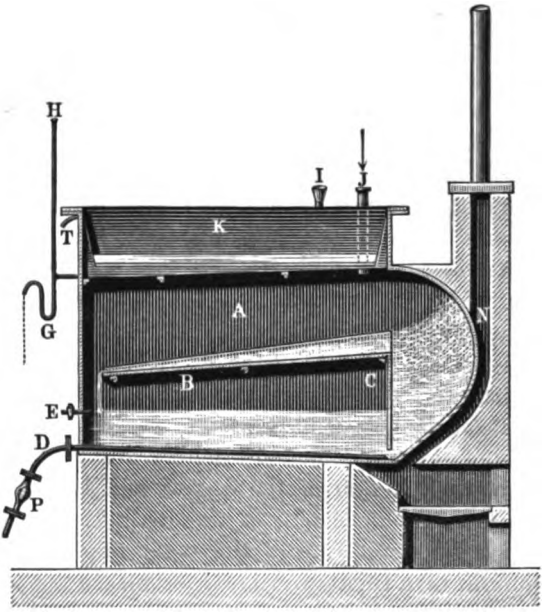
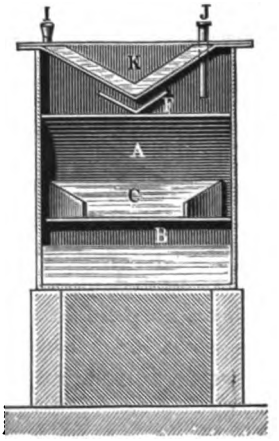


Fig. 54.



out at T; a gutter F receives the liquid condensing from the vapour upon the lower side of K. The tar is introduced through J, and at first takes its level in both compartments, as regulated by the tap E. As it is heated in the smaller compartment alone, it swells up there, rises, and at last gets up to the slanting plate B, on which it spreads out, is cooled down, and runs back into the larger compartment, whence it flows back into the smaller compartment, where it again swells up and overflows on to B, so long as any water is present. The vapours of steam and light oil which are formed condense, on touching the cooled cover, into a liquid which falls into the gutter F, and is carried out of the still by the siphon tube G; the gases escape through H. After some time the circulation becomes slower; the tar ceases to froth and swell, and becomes hotter. It is now perfectly quiet, and can be run off through D and P into the ordinary stills, where it is distilled without any bumping or danger.

W. Maxwell (B. P. 3640, 1882) places vertical pipes within the still, with or without the use of a compressed-air tube, for the purpose of facilitating the separation of water, oil, and other liquids from tar while undergoing distillation.

Previous Purification of Coal-tar.

E. Jacobsen * proposes purifying the tar previous to its distillation. If coal-tar be mixed with half its volume of carbon bisulphide, all the free carbon will separate as a powder; and if the liquid be decanted, the carbon bisulphide blown off by steam, and the residue mixed with petroleum-spirit, all the brown asphalt will be left behind, whilst the remaining liquid, the petroleum-spirit having been steamed off, will consist of an orange-coloured clear oil containing naphthalene, anthracene, &c. Similarly, coal-tar pitch can be purified from its carbonaceous and asphalty portions; the hydrocarbons remaining over are more easily fractionated, and less of them is gasified on heating, so that anthracene can be recovered from them with more facility. Carbon bisulphide and petroleum spirit are easily recovered without any essential loss (?). When petroleum-spirit is added directly to coal-tar, the asphalt, which is precipitated, forms, with the free carbon and a portion of the dead oil, a tough, difficultly manageable mass; and by adding a mixture

* Chem. techn. Repertorium, 1869, ii. p. 107.

of carbon bisulphide and petroleum-spirit, part of the brown asphalt is dissolved. Hence the process should be carried out just as above described. I am not aware that this process has ever been carried out on the large scale. It seems too expensive and too dangerous as regards fire, and probably a good deal of anthracene will be left in the "free carbon" and the "brown asphalt." Neither would it be easy to obtain the benzol free from carbon bisulphide.

Construction of Tar-stills.

Only one material is suitable for tar-stills, viz. wrought iron. Cast-iron stills would be less subject to burn away and to mechanical injury in clearing them of coke; but they cannot be easily made of a considerable size. Both the difficulties and the cost of casting increase very rapidly with an increase in the size of hollow objects; neither can a perfect uniformity of structure be expected in the case of unusually large castings.

Even when they are made as upright loam-castings and with a large feeding-head, an air-bubble may very easily remain, and, in the case of vessels exposed to a direct fire, cause in that place a most dangerous tendency to crack. But even a faultless casting is still very much exposed to cracking, and must never be set without a curtain arch over the fireplace: nevertheless any carelessness of the fireman will cause it to crack; and the mischief will then be great in proportion to the size of the vessel. Wrought-iron vessels, on the other hand, cannot be cracked by incautious firing, at least not in consequence of sudden changes of temperature, although an explosion from an excess of pressure, if all outlets are stopped up, is still possible. It is true that the plates are more easily burnt by the first action of the fire than cast-iron; but this must, under any circumstances, be provided against by a curtain arch. It takes very gross and long-continued carelessness on the part of a fireman to burn the plates of a properly set still, whilst even the best workman cannot always help the cracking of a cast-iron still.

It should be further noticed that the metal of cast-iron stills must be at least four times as thick as the usual boiler-plates; this makes the former much more expensive than the latter, and increases the consumption of fuel. Lastly, wrought-iron stills can

be repaired by patching, or by putting in fresh plates, whilst similar repairs are nearly always excluded in the case of cast-iron.

If wrought-iron stills are protected, by means of a curtain arch, from injury by the first heat of the fire, they last very long, provided they are properly treated, especially in cleaning out. A new still should go at least four years without any great repairs, and as long again after each thorough repair. The plates burn through most easily at the bottom, where the flame issues from underneath the curtain arch, if the latter does not reach right through. Where this is the case, so that the still-bottom is not touched at all by the flame, and is only as it were in a hot-air bath, the stills may last much longer than the above-mentioned time.

The following general rules should be observed in constructing the stills. The *thickness of the plate* as a rule need not be over $\frac{3}{8}$ inch; the very greatest, for forty or fifty tons of tar, should be $\frac{1}{2}$ inch. The top plates should be quite as thick as the bottom plates, since they wear out rather more quickly (see below).

Of course the plates must be very well riveted and caulked; but in spite of that the seams of new stills often show a tendency to leak at the end of the distillation, when the temperature has risen very high. This is seen by a flame running along the seams or rivets; it always occurs at the bottom, and can be cured by fresh caulkings. Even without that, coke soon sets into the seams and makes them tight; hence such leaking is mostly noticed after a thorough cleaning of the stills. In any case it does not endanger the safety of the still. The same thing holds good of the stills for light oil and other similar ones, to be mentioned hereafter.

Much difference of opinion exists as to the best *shape of a tar-still.* Formerly any thing was made to do, especially old steam-boilers of various shapes. Mostly this was bad economy; increased consumption of fuel, longer time of working off, frequent repairs, and frothing over of the contents of the still amounted to several times the cost of a new tar-still of the best pattern. But there is much dissension upon the question, What is the best pattern for a tar-still? The following is a description of the various forms of stills found by me in 1880 at well-conducted works in different countries.

That shape of still which is met with almost universally in England, and which I have seen at the majority of German

works also, is an *upright cylinder*, of nearly equal height and diameter, with a dome-shaped top and a concave bottom, *i. e.* equally curved upwards in a dome-shape. This concave bottom is preferable to a flat bottom, on account of its greater stiffness and larger heating-surface, and because the iron can better expand and contract with the inevitable great changes of temperature to which it is exposed. Convex bottoms would have equal advantages, but would not present such a favourable proportion between the heating-surface and the contents of a boiler as concave ones; they are not so easily set, and the pitch could not very well be run out completely by means of a cock in the deepest part.

Such stills are always made of considerable size, both to save labour for attendance and because the separation of the products according to their boiling-points is easier the larger the quantity treated in each operation. Rarely are smaller stills used than those for a 6-ton charge; but they are sometimes preferred, because a charge can be worked off in 10 or 12 hours, and night-work thus becomes unnecessary. But the large works usually have larger stills :—in England, holding from 10 to 20 tons, rarely more; in Germany, 20, 25, or even 50 tons. It is doubtful whether such very large stills are the best; 20 tons seems the most convenient size.

Watson Smith advises trying the tightness of each still by putting it on its seat, connecting it with a steam-boiler, closing all openings, and blowing in steam at $2\frac{1}{2}$ atmospheres' pressure; it should not leak anywhere then. (Evidently an air-cock must be left open till all the air has been expelled.) He also observes that there is usually some difficulty in fixing the cast-iron still-head, inasmuch as the cover is mostly made of several pieces overlapping each other at the seams, and thus presenting obstacles to a tight joint with the flange of the still-head. This can be avoided, either by making the top piece out of one plate, with a circular opening for the head; or else, if the top is constructed of several pieces, by making a wrought-iron ring to fit the central opening (previously provided with rivet-holes), hammering it down while red-hot, so hot that it adapts itself to all the uneven places of the joints, marking the places for the rivets, taking the ring off, punching the rivet-holes, putting the ring on again, and riveting it fast to the top. The inner border of this ring, projecting into

the central opening and left quite smooth, serves for bolting on the still-head.

The usual *cement* for tar-stills is the ordinary rust-cement, made of iron borings, sal-ammoniac, and sulphur, moistened with a little ammoniacal liquor. Watson Smith recommends a cement made of 2 parts iron borings, 2 sifted quicklime, 1¼ common salt, ½ flowers of sulphur, well mixed up and made into a paste with ammoniacal liquor. When it has set and has been exposed to the heat of the still, it turns very hard and resists the fire very well.—Instead of cement, it seems preferable, wherever possible, to employ asbestos packing, which is well-nigh indestructible, but rather porous, if employed in thick plates.

Some works employ a very different shape of still, viz. *horizontal cylinders* similar to steam-boilers. They are of course less in diameter (rarely above 7 feet), but longer, than upright stills. It would seem that they require more fuel than the latter form of stills, and that the tar has much more tendency to froth over in them during the first period of the distillation.

At a German works the author found such horizontal stills, holding 18 tons and provided with two or three still-heads, which were pronounced to work very satisfactorily. At another works he saw horizontal stills, holding 22 tons, which required 48 hours for distilling off a charge, apart from the time for filling and cooling down, so that only two charges could be made per week. The plates have a thickness of 12 millimetres at the bottom, and 14 millimetres at the top (that is, slightly below and slightly above ½ inch). They are made thicker at the top, because they suffer more where they are not in contact with tar or pitch, and are more reduced in thickness by working than the bottom plates—an observation which I have found confirmed in the case of English upright stills. The setting of the horizontal stills is best made in such a way that the flame does not directly touch the bottom of the still for about two thirds of its length, but is kept off by an arch perforated with pigeon-holes; the last third of the bottom is heated by the direct flame, the bottom of the flue being 12 inches below the lowest part of the still.

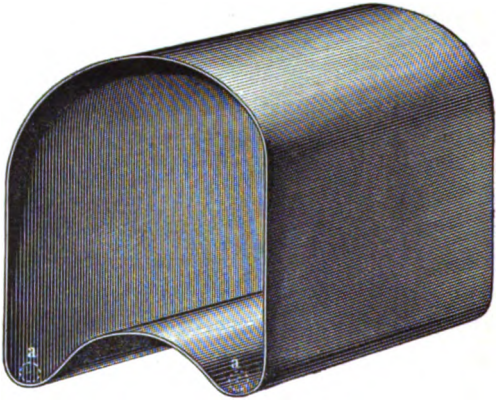
In America the most usual shape of tar-stills is also that of horizontal cylinders, made of $\frac{5}{16}$ inch steel plates, of about 2000 gallons capacity, with only one row of rivets along the top.

In my opinion, horizontal stills are altogether inferior to

upright ones; they work much more slowly, and they consume incomparably more fuel than the latter. At a works where horizontal stills are used, the manager told me that 1 ton of coal, or an equivalent of other fuel, would distil 5 tons of tar; whilst at several other works, where upright stills are used, I found that only *one third* of that amount of fuel was consumed.

Stills of a very peculiar shape are employed at the Paris gas-works. They are *waggon-shaped*, with an incurved bottom, and edges very much rounded (fig. 55), holding only 1440 gallons of tar. The flues run twice round the sides of the stills. This shape, I am informed, is preferred because it causes the least

Fig. 55.

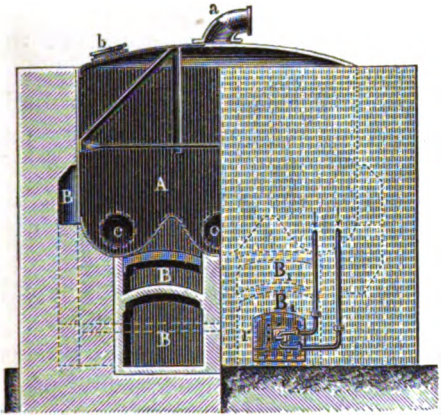


injury to the metal in contracting and expanding with the changes of temperature. But such injury has not been observed where the usual upright cylindrical stills are at work; and the Paris shape has from the first the disadvantage of requiring two running-off cocks, one for each side (at *a a*). These stills are set so that the bottom is not touched at all by the fire, which circulates twice round the sides. In the lower flue the flame does not impinge directly upon the metal, which is protected by thin firebricks; in the upper flues these are wanting. Everywhere else I have found the flame (which has expended its greatest heat upon the curtain arch beneath the still-bottom) heating

the sides of the still without any firebrick lining and without doing any injury to the still. The stills at those works do not show the arrangements mentioned by Girard and Delaire* and by Wurtz†, by which, as soon as the level of the tar sinks too low, the upper flue is shut off and the fire is only allowed to circulate in the lower flue. But anyhow the flues heat only the lower part of the still; so that such a complicated arrangement is not called for. Even the upper flue is built in such a way that the level of the pitch at the end of the distillation is still above it —which is not very difficult to manage, since the bulk of the pitch is at least half of that of the tar.

Another shape of waggon-still is shown in figs. 56 and 57,

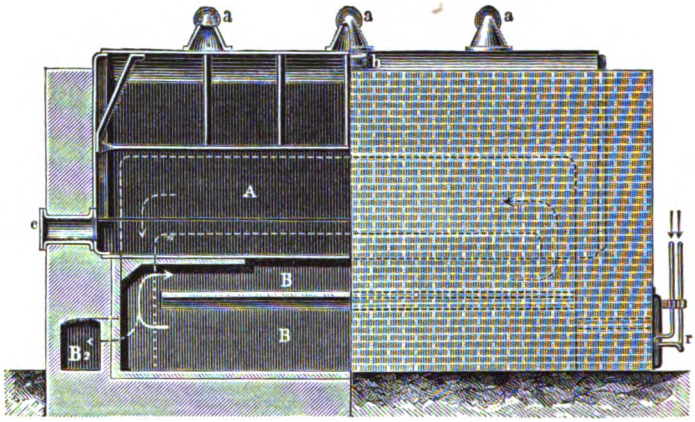
Fig. 56.



according to Engler (Dingl. Journ. 1886, vol. cclx. p. 435), as employed in the Baku petroleum-refineries. They are up to 23 feet long, 13 feet wide, and 10 feet high. *a a* are the still-heads; *b* a man-hole; *c c* three outlets for the residues. The arrangement of the internal stays is clear from the diagrams. There are two fireplaces, *r*, supplied with liquid residues (p. 174 *et seq.*; I have seen tar-stills worked with creosote-oil, when this was unsaleable!); the flame first passes through the arched-over flues B, B_1, returns at the still-end to the fore part, rises up, travels again backwards

* Dérivés de la Houille, p. 8. † Matières colorantes, p. 23.

Fig. 57.



along the sides of the still, then downwards and through the flue B_2 into the chimney.

Lennard has patented a still, forming a cylinder 20 feet by 7 feet 6 inches, provided with an agitator, and set in a furnace with three fire-doors*. E. Berninghaus also recommended a horizontal still, with a stirring-apparatus resembling a ship's screw (G. P. 4586). Another horizontal still, with agitators as used in Scotland, is shown later on in fig. 72.

The various parts belonging to a tar-still are best described along with an explanation of figures 58 to 60. These represent a 25-*ton still*, the details of which, as well as those of the setting, are not copied from a particular plant existing at a factory, but combine those features of all the apparatus observed by myself in England and Germany which seem to me most practical. But each single part, described or drawn here or hereafter, is actually in use at one or another of the largest and best works.

Fig. 58 is a cross section along the line E F of the plans; fig. 59, a plan laid through C D of fig. 58; fig. 60, a plan of the still itself, along the line A B of fig. 58,—all $\frac{1}{50}$ of the natural size. The still is 9 ft. 10 in. wide, and 11 ft. 6 in. high (without the dome), made of $\frac{3}{8}$-inch or $\frac{1}{2}$-inch boiler-plate. The inward curve of the bottom is about the same as the outward curve of the top: both of them are sometimes made much higher than shown here.

* Journ. Soc. Chem. Ind. 1883, p. 239.

Fig. 58.

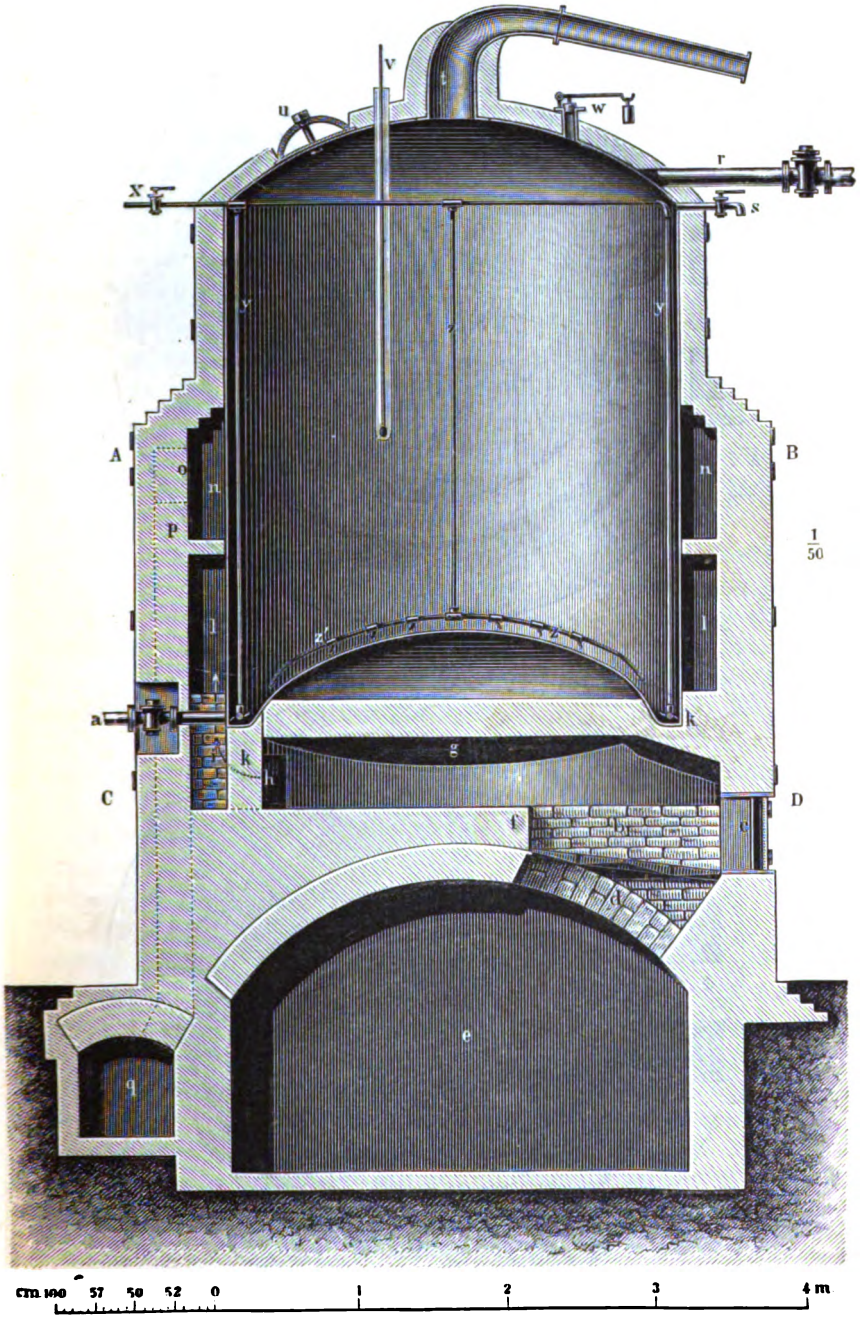


Fig. 59.

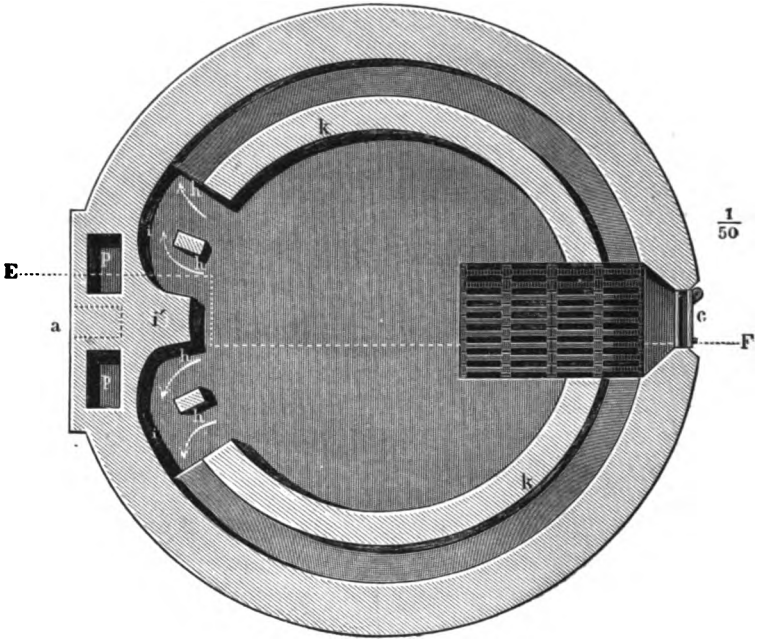
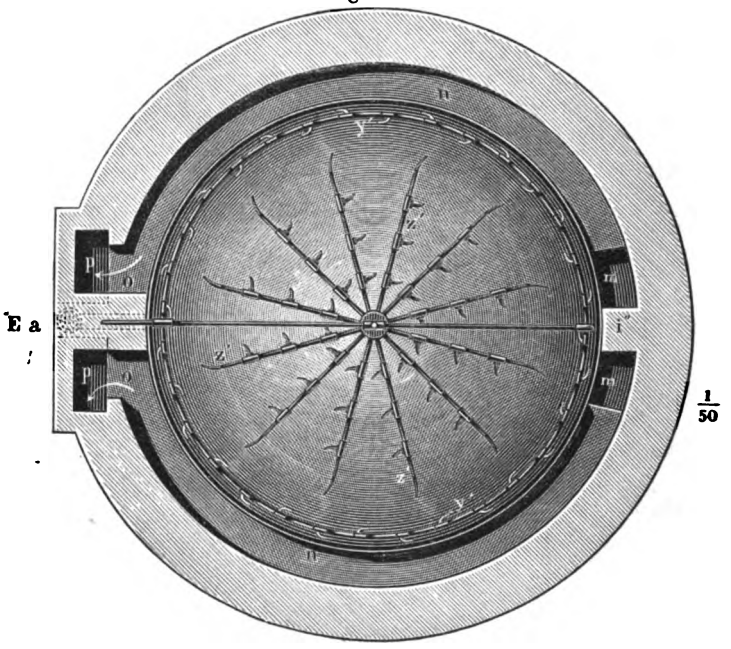


Fig. 60.



The still may be set with a slight slope towards the outlet-cock *a*, which in any case is placed as nearly as possible just above the bottom, or even in the flat part of it. This is absolutely necessary if hard pitch is made; where only soft pitch is made, as is usual in Germany, it is not so essential.

The still is heated by a fire-grate, *b*, adapted to the special quality of the fuel. The usual fuel is small coal (slack); sometimes, especially at gas-works distilling their own tar, coke is employed, by which, however, the still-bottom may be injured unless completely protected by a curtain arch, or unless steam be introduced at the end of the operation. Sometimes, if the heavy oil is not easily saleable, it is employed for firing the tar-stills; many arrangements for this purpose have been described in the 4th Chapter.

The fireplace is accessible from without by a door, *c*. Where there are a number of stills, all the doors are arranged in the same lines, opposite to the side where the pitch-cocks *a* are placed. Usually the ash-pits under each grate communicate with the outer air by an opening below the fire-door. But in our diagrams is shown the arrangement at one of the largest English works. Here the ash-pits are closed below the fire-doors, and all of them communicate by an opening, *d*, with a large overarched passage, *e*, running along the whole set of stills and only accessible from the two extremities; this affords perfect security against fire in case of the tar boiling over and running out of the receivers. It is true that other precautions can be taken against this danger, such as constructing the receivers in the manner to be described below, where the tar, even if it boils over, cannot get at the still-fires; but the arrangement shown here will also act in the case of accidents to the pipes and, especially, to the still-head, for with it the vapours issuing in great force cannot take fire at the ash-pits. Moreover the underground passage *e* permits great cleanliness. It is useful to place a steam-pipe below each fire-grate, to increase the draught, to prevent overheating of the grate-bars and the fire-bars, and thus to avoid the formation of fluxed cinders.

The flame travels over the fire-bridge *f*, and under the arch *g*. This arch is sprung barrel-shaped from the annular wall *k k* on which the still is seated, and completely shuts off the still-bottom from the flame. Thus the space between *g* and the still-bottom

is an air-bath, kept very hot by the flame below *g*, but never excessively so. So much heat is imparted to the arch *g*, that at the end of the operation no firing is needed, especially if steam or exhaustion be applied. The weight of the still resting upon the annular wall *k k* enables this all the better to support the pressure of the curtain arch *g*, which is otherwise independent of the brickwork of the fireplace, and can be easily renewed when it is too much burnt out. The flame now travels on through four holes, *h h*, into two vertical flues, *i i*, and arrives at the cylindrical shell of the still. The solid pillar *i'*, between the flues *i i*, is continued to the top. Through this pillar passes the pipe connecting the pitch-cock *a* with the still, protected from the fire, but kept warm by the flues *i i* and *p p*. The pillar *i'* forces the flame to divide into two currents, which pass round the lower part of the still in the annular flue *l l*, are prevented from uniting in front by the pillar *i''*, pass through the flues *m m* into the upper annular flues *n n*, return to the back part, and enter through *o o* into the downcast shafts, *p p*, communicating with the main flue, *q*. The shafts *p p* are provided in suitable places with dampers, by which equal heating of both sides of the still can be secured. For shallower stills a single annular flue would be sufficient; its downcast shafts would have to be arranged in front, at each side of the fireplace. The best width of the annular flue is from 9 to 12 inches.

The outer wall, as far as the flues reach, should be at least 14 inches thick, and should be strengthened by several iron bands, shown in fig. 58. Above the flues the still is surrounded by a 9-inch brick jacket to prevent cooling; the brickwork continues along the whole top, and preferably also up to the top of the still-head *t*. Such a protection against cooling is all the more needed if the tar-stills are under the open sky, or merely covered by a light corrugated iron roof, &c. This, the most usual, style causes any explosions or fires to be less destructive than if the stills were placed in a substantial building. It is advisable in that case to protect the brickwork of the stills against rain by a coat of molten pitch.

The *mountings of the still* are as follows. A cast-iron *supply-pipe*, *r* (fig. 58), closed by a slide-valve or cock, is provided for running-in the tar. It is best rather wide, say 6 inches, so that much time may not be consumed in filling the still. Where the

tar is not pumped, but run in from a high store-tank, a simple hole will do, afterwards closed by a screw-plug, or even the man-hole. There may be a special hole, through which the depth of the tar can be gauged; but preferable is an *overflow-cock*, *s*, of 1-inch bore. As soon as tar comes out of it the feeding is stopped and *s* is closed. We have seen on p. 197 that, during the heating up, the water collecting on the top of the tar can be removed from time to time by opening *s*, which greatly assists the work.

The cock *a* (fig. 58) serves for *running off the pitch*; it will be described more exactly hereafter. Instead of connecting it, as is here shown, by a 4-inch pipe with the still, the latter is sometimes provided with a 12-inch pipe projecting through the brickwork, and in this the cock *a* is fixed. If the setting is similar to that shown here, the pipe is always hot enough for the pitch to remain liquid. But it is possible to work altogether without a cock, by forcing up the pitch through a vertical delivery-pipe by means of steam (compare below).

The vapours are conducted away by the cast-iron *still-head t*, which decreases in width from 12 inches down to 6 inches, and is then continued into a 6-inch metal pipe leading to the condensing-tank. Sometimes a gutter is provided inside the still-head, at its base, to conduct directly outwards any liquid condensing in the rising part of the head, so that it cannot drop back into the still, where it might cause frothing-up; but this is hardly necessary if that part of the still-head be surrounded by a bad conductor of heat. In some places they put a steam-pipe into the still-head, in order to remove obstructions by blowing through it. But a still-head of such a width cannot very well become obstructed, if it has a little fall. As to the connexion of the still-head with the still-top, we have described it on p. 202.

Every tar-still must have a *man-hole*. We have represented this at *u* (fig. 58), like a steam-boiler man-hole, closed by a cover fixed on by an arm and screw-bolt; the joint can be made good by plastic clay, or else by a ring of asbestos packing. But in some places the manhole-lid is made to serve at the same time as a *safety-valve*. It is then a plate, loosely laid upon a riveted neck, and joined to it merely by some cement which does not become too hard. If the pressure within the still should for some reason or another mount too high, the lid will be thrown off before

any other damage can occur*. In America some tar-stills are provided with a steel pin loosely fitting into a hole in the still-cover; when there is pressure in the still, the pin is ejected, vapours issue from the hole, which is a sign for opening the fire-doors and blowing steam through the worm. Unless some such contrivance is provided, there should be a proper safety-valve present, as delineated here at *w*; but many tar-stills are found without such. A very useful precaution consists in providing a side branch to the safety-valve, which permits any tar that boils over to run to some safe place away from the still. Lastly, a *thermometer*, *v*, should be placed in an iron tube closed at the bottom and filled with iron filings or mercury; it should reach halfway down the still. In lieu of this, some works have pyrometers of various constructions, mostly not very reliable in their indications. Unless steam be applied in the last stage of the process, a mercurial thermometer cannot be used, since mercury boils at 360°; in that case it must first be taken out of the iron tube. It should not be forgotten that mercurial thermometers which have been exposed to a high temperature for some time vary their fixed points considerably, owing to deformations of their bulbs; such variations have been observed to extend to as much as 14°. Hence they must be compared with a standard thermometer from time to time; otherwise mistakes in the working and disputes with buyers may occur. This of course holds good of all thermometers used at tar-distilleries.

The reader will notice in our diagram (fig. 56) a system *of steam-pipes, x y z*. We shall see afterwards that the majority of works now employ steam, mostly superheated, for finishing the process. This is usually done by means of a cross-shaped tube with perforations for the issue of the steam. Here we have shown the more perfect arrangement patented by Trewby and Fenner (No. 3613, Sept. 9th, 1879). The steam is introduced by a 1-inch pipe with tap *x*, which sends down three vertical branches *y z y* inside the still. The tubes *y y* communicate with an annular-shaped tube *y'*,

* Watson Smith (Journ. Soc. Chem. Ind. 1882, p. 342) doubts whether this contrivance would be efficient—either it would be too tight, and thus not act at all, or else it would be too loose, and thus allow vapours to escape at the end of the process. But I am acquainted with a very large and excellently managed tar-works where the above-described arrangement has worked perfectly for a long time.

placed in the lowest part of the still, and z with a system of branch pipes $z' z'$, covering the whole still-bottom. Both y' and zz' are provided with a large number of open, slightly bent outlet-pipes with contracted ends. Thus the steam is divided into many thin jets, ranging all over the bottom of the still, which prevent its overheating and carry away the vapours of the heavy hydrocarbons. Owing to the large surface of the steam-tubes, the steam is superheated before issuing, and a special superheater is unnecessary.

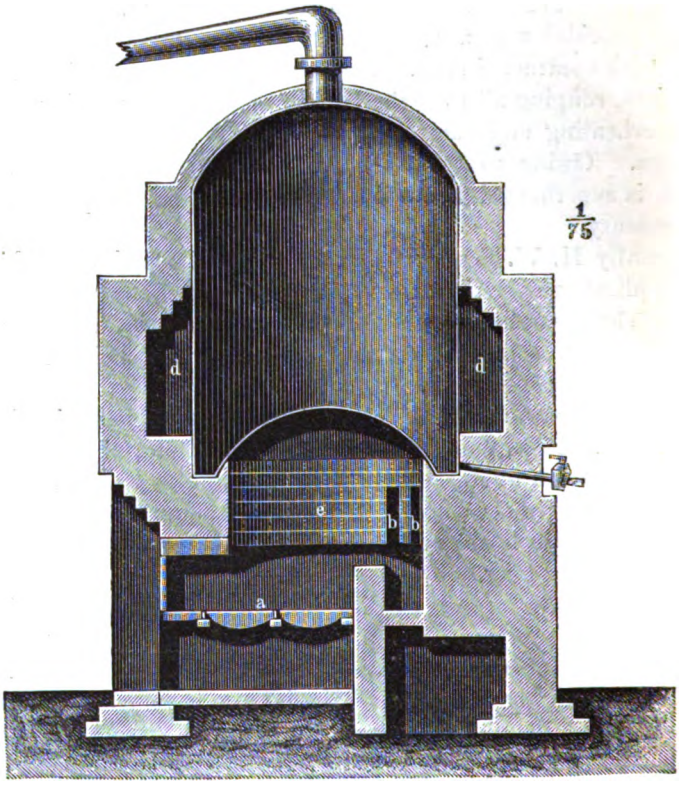
Recently H. W. Fenner (B. P. 13,629, of 1884) has combined the application of stirrers with that of steam, by providing a hollow shaft, passing down the centre of the still, with branch pipes for distributing the steam, the whole system being made to rotate by suitable gearing.

One of the usual ways of setting tar-stills in England is shown in fig. 61 *. Here there is no curtain arch at all; the fire of the grate *a* passes through the holes *b* in the annular wall *c*, and once round the still in the flue *d*. Sometimes the annular wall which supports the still is strengthened by iron bearers, which probably do not last very long.

At one of the largest English tar-works I found stills of the shape sketched in fig. 61 A (p. 215), which have been working there for a number of years and give the fullest satisfaction. It will be noticed that the rise of the bottom is very much greater than in the stills already figured, so that, in fact, the crown of the bottom dome is quite halfway up the cylindrical portion of the still. This causes the heat of the fire to penetrate well into the interior of the mass of tar or pitch, and keeps the level of the pitch at the end of the distillation at a convenient height above the flue. These stills hold 14 tons of tar, and require 16 hours before running off the pitch, so that they can be charged fresh every day. In lieu of a running-off cock or valve there is a pipe *a* reaching down to the lowest part of the still, and continued outside in a cock *b* and a branch *c*, descending into a closed tank *d*. At the end of the distillation, and after the pitch has been softened, as may be required, by pumping tar-oils back into

* From 'Chemistry Applied to the Arts and Manufactures,' by Wm. Mackenzie, vol. i. p. 499. The other figures found in the same place, taken from Bolley's 'Technologie der Gespinnstfasern' (p. 210 *et seq.*) do not refer to the distillation of coal-tar, but of browncoal-tar.

Fig. 61.

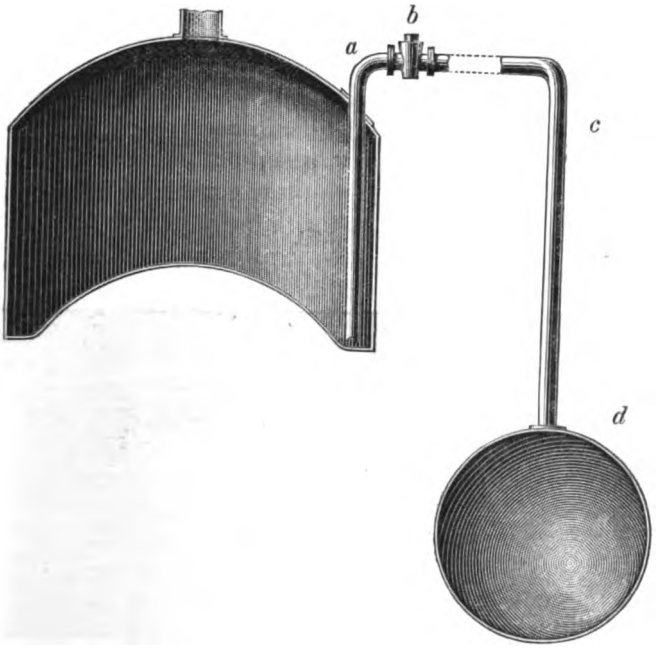


the still, a vacuum is produced in *d*, and after opening the cock *b* the pitch will rise through *a* and *c* and flow into *d*.

These stills require only one ton of coal, or half a ton of creosote-oil, for distilling the whole charge (14 tons) of tar.

Similar stills are used at another of the very largest English tar-works; they hold 10 tons. Recently some stills have been made there to hold 20 tons, keeping to the same horizontal section and to the same curve of top and bottom, and merely making the cylindrical portion so much higher; there seems to be a saving of fuel in the latter case. The 10-ton stills require 12 hours for distilling, 3 hours for cooling down till the pitch can be run off, and another 4 hours for filling. The firing is here (as in some other works) exclusively done by means of creosote-oil, of which

Fig. 61 A.



only 50 to 60 gallons are consumed for working off a 10-ton still, which must be considered a very good result.

From a communication kindly made to me in 1885 by Mr. John Wyld, of the Bradford Corporation Works at Frizinghall, it appears that at one or more works in that neighbourhood the system of firing by gas-producers was applied to tar-stills, but it is not stated whether it was found to possess any advantage. There is no reason why it should not answer; the regulation of firing would be much easier therewith; but I should not expect to find any saving of fuel by that method.

H. W. Fenner (B. P. 13,630, of 1884) forces the flame to touch the bottom and sides of the still in a particular manner

Condensing-Apparatus.

Girard and Delaire (*loc. cit.* pp. 8 and 10) state that sometimes a still is provided with three condensing-worms, each regulated by a stopcock, and employed one after another for the different

fractions. None of the works known to me employ that kind of apparatus, the object of which is not very clear, since the separation of the fractions need not commence in the worms, but can take place in the receivers. I have never observed more than one condensing-worm; but these are of a very different description. The English works mostly employ cast-iron pipes, in lengths of 9 and 6 feet, from 4 to 6 inches wide, and connected by elbow-pieces (figs. 62 and 63). The whole is contained in a wrought-

Fig. 62.

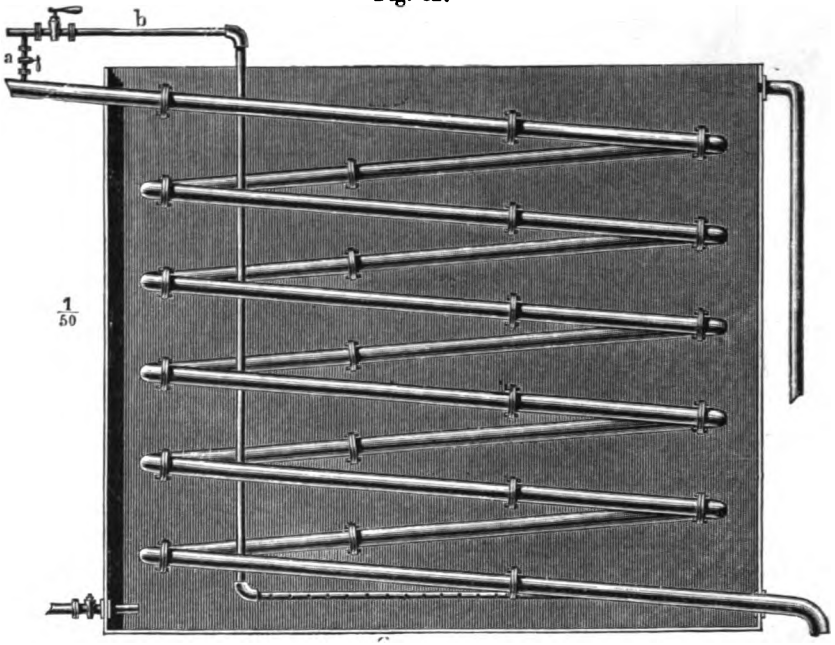
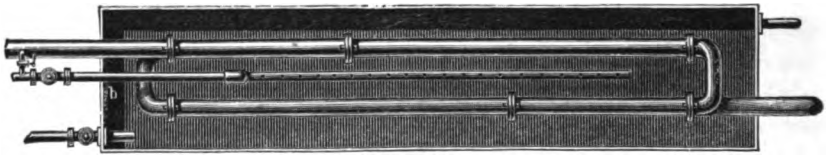


Fig. 63.



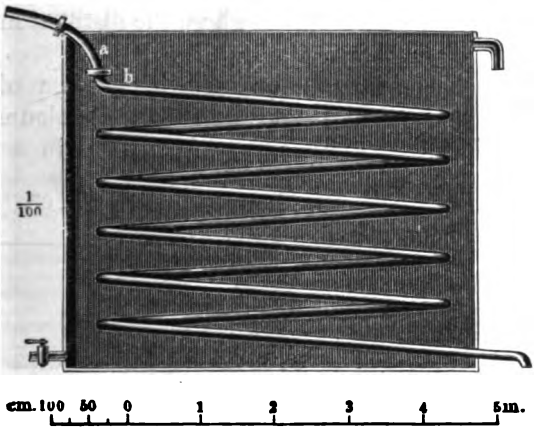
iron tank, and is supported by strong iron stays (not shown in the diagram). As the tank would be rather narrow, sometimes two worms, belonging to different stills, are placed in the

same tank. Formerly the elbows were sometimes provided with cleaning-out holes; but these are quite unnecessary, if the pipes have enough fall and if the tank at the end of the process is kept warm. But it is always advisable to put a steam-pipe *a* in the top pipe, so that the worm can be purified by blowing steam through it in case of need. In any case there should be a steam-pipe (*b*) for heating the water surrounding the worm.

At some English works the horizontal section of the cooling-system is not, as here shown, oblong, but square; this entails the use of very large water-cisterns to contain the worm.

The German works prefer worms made of wrought iron or even of lead. In the latter case the cast-iron pipe *a* coming from the still (fig. 64) must be continued at least a foot below the level of

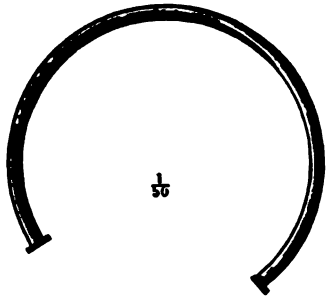
Fig. 64.



the cooling-water, and the lead-pipe *b* commence there; otherwise the latter might easily be melted at the end of the process by the heat of the vapours in the part not cooled by the water. We cannot see any reason for recommending lead worms for tar-stills.

The majority of German works prefer drawn wrought-iron tubes of 2 inches bore, bent in the shape of a three-quarter circle (fig. 65) and connected by screwed-on flanges. With these there are no uneven places at the joints and no sharp angles as with the cast-iron worms. Even better than those tubes are wrought-iron worms each made in a single piece, as supplied by some

Fig. 65.



Rhenish ironworks. These worms are always contained in circular iron tanks provided with a steam-pipe. Wrought-iron or lead worms cool better than cast-iron ones, owing to the less thickness of metal. Their narrowness is a drawback, which is, however, of not much importance where the distillation is carried on by the help of a vacuum.

Engler (*loc. cit.*) describes the following system of cast-iron refrigerators, frequently used at the Baku petroleum-refineries (figs. 66 and 67). There are always four pipes in a horizontal

Fig. 66.

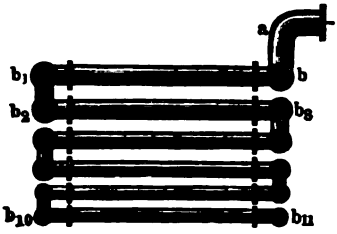
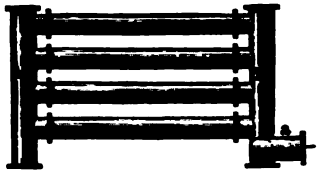


Fig. 67.



plane, joined by a cross-piece b, b_1, b_2, &c., and six such systems above one another, altogether 24 pipes, with a total length of 200 to 300 feet; the top pipes have a width of 8 inches, the middle ones 7 inches, and the bottom ones 5½ inches. The vapours enter through a, spread on the cross-piece b, pass across through four pipes to the second cross-piece b_1, then downwards to b_2, back again through four pipes to b_3, and so on down to the outlet at b_{11}.

The total length of condensing-pipes is calculated in England at from 140 to 200 feet per still. In Germany the refrigerators are about 7 feet wide, and from 7 to 10 feet deep, with narrowly

coiled worms, making the length of pipe from 200 to 300 feet, according to the size of the stills.

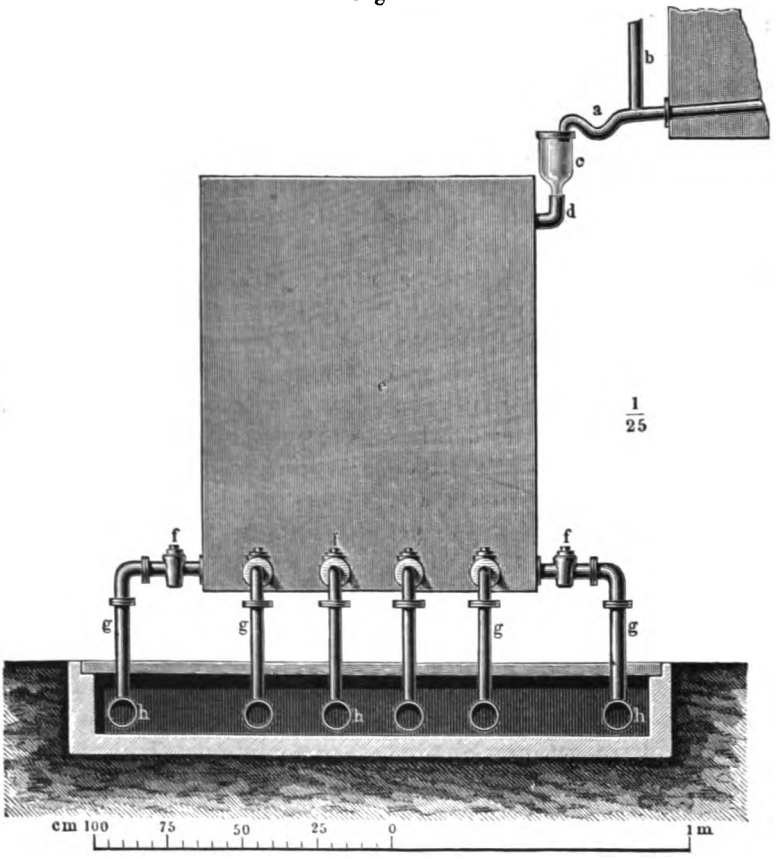
As *cement* for the joints the ordinary rust cement (made of iron borings, sulphur, and sal-ammoniac) can be employed. In lieu of this another cement may be used, which is as tight, but is more easily removed again. It is made by slaking lime to a powder, which is sifted and then kneaded with a little water to a stiff dough-like putty. This lime-putty is stemmed into the joints, hardens in 24 hours, and is perfectly tight against water and oils, either liquid or in the state of vapour; nor does heat affect it; only it must not be exposed to direct fire. For joining flanges, asbestos packing is no doubt the best possible material.

Instead of a condensing-worm, some employ a double cylinder with a current of water in the annular space between the cylinders. Such a contrivance is evidently safe against being stopped up.

Where the condensing-pipe comes out of the tank, it is slightly bent upwards (fig. 68 at *a*); and at this place an upright pipe *b* is fixed, through which the permanent gases escape, whilst the liquid products run into the receivers. We shall see later on that the escaping gases ought not to pass directly into the atmosphere, but first through some purifying-apparatus.

In order to separate the different products, there must be a corresponding number of *receivers*, and the products running out of *a* must be run at discretion into any of these. Evidently very many contrivances may serve for changing the receivers; but some points must be always observed. Thus the receivers for the first products must be tightly closed, to avoid both loss and danger of fire. Furthermore, the first receiver must be provided with some contrivance for easily separating the oily and watery portions. The receivers for carbolic oil and those for heavy oils must be easily accessible, in order to remove the crystalline masses always separating in them. Above all, it is imperative to take every possible precaution against fire. If the receivers are placed near the tar-stills, they must be separated from them by a solid wall. Any tar which might by accident boil over and run out of the receivers must under no circumstances be able to get near the still-fires or any other fireplaces. At some places the receivers are only just large enough to hold the product of one operation. This has the advantage that the manager can judge of the still-work by the depth of the liquor in the receivers; but then there

Fig. 68.

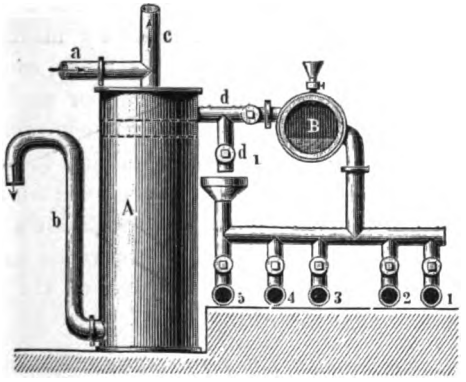


must be another and larger set of store-tanks for each fraction. Hence the receivers are frequently at once so constructed as to contain a large quantity of products, in which case they are placed at some distance from the stills and serve for a number of these at the same time.

Instead of dwelling upon the various ways in which receivers can be arranged, we prefer describing a special arrangement found at some of the largest works, and fulfilling the conditions of cleanliness, convenience, and safety. The distillates of each still run from the swan-neck pipe *a* (fig. 68) into the glass jar *c*, in which the process can be well observed. A jar with hydrometer can be placed in it; samples may be taken from it; the rate of distillation

is easily observed; the appearance of the products is noted, &c. When the oils get too hot, it can be replaced by an iron funnel. The glass jar *c* is closed by a sheet-iron cover, cut out for the passage of the pipe *a*. It is fixed into an elbow-pipe *d*, which conveys the liquids into the tight box *e*. To this are attached as many cocks *ff* as there are different fractions to collect. These are simple 2-inch gas-cocks, made of cast-iron; brass cannot be employed, on account of the ammoniacal liquor. The cocks for creosote-oil and anthracene-oil may be larger, say, three or four inches bore. The cocks *ff* (in our diagram there are six) are connected by flanges with the pipes *g g* which form vertical branches of the main pipes *h h*. The latter are laid in a bricked pit running along the whole set of stills, so that the products from all the stills pass into these pipes, which convey them ultimately into the store-tanks for each fraction. Care must be taken that the pipes *h h* have sufficient fall, and that the later distillates are not too much cooled in them, which would be sure to stop them up with naphthalene, &c. Such cooling is partly prevented by covering over the pit with planks; but it is safer to put steam-pipes into the pipes conveying the later distillates. A special cock in the bottom of the collecting-box *e* permits samples to be taken and the contents to be run off at will. It is also possible to adapt this box to a continuous separation of the ammoniacal liquor; but this is an unnecessary complication, and it is more advisable to let this separation take place in the receivers.

Fig. 69.



A similar arrangement is shown by Engler (*loc. cit.*), and is

represented in fig. 69. The oil and water run through *a* into the cylinder A, where they separate. The water runs off through *b*; the gases escape through *c*; the oil runs through *d* into the "lantern" B, where the glass pane permits observing its colour &c. From this point the oils are carried on through the taps 1 to 5 to the different receivers; the last, and heaviest, oils do not pass through the lantern, but straight into No. 5 through the tap d_1. This apparatus, which is used in refining petroleum, would require some modifications if it were to serve for distilling coal-tar.

The *receivers* or *store-tanks* for the various fractions may be of any shape—square, cylindrical, &c. They are always made of wrought iron, and should be very well riveted and caulked; otherwise, especially if placed on the ground or even underground, great losses by leakage may occur before any thing is noticed, which may even seriously contaminate neighbouring wells and watercourses. Even a previous testing with water will only reveal coarser leaks, as tar-oils penetrate much more easily through the joints than water. Hence the vessels must be closely observed for some time; if they are sunk in the ground there must be a free space left all round them for some days after they have been first taken into use, so that any leaks may be found out and stopped before the earth is filled in. The bottom of the vessels ought always to be formed of one piece. Of course the needful precautions against corrosion by rusting must be taken.

At some works, steamboiler-shaped cylinders (either horizontal or upright), which can be used at the same time for *forcing-up the oils by air-pressure*, are preferred as receivers, or at least as store-tanks. Instead of pumping the liquids by means of ordinary pumps, which is very inconvenient with tar-oils, owing to the impossibility of employing fatty or india-rubber packings, they are now nearly always pumped by air-pressure, compressed air being conveyed from an air-pump or blowing-engine to each of the receivers. This air presses on the surface of the oil and forces the liquids through ascending pipes, which reach down to the bottom of the vessel, and are provided with stopcocks, to any suitable height or place. Hence the moving parts of the machinery are nowhere in contact with the oils.

Treatment of the Gases.

We have already mentioned the permanent gases formed in the distilling process. They are partly combustible; but it will hardly ever pay to utilize them in this respect, especially as that would entail considerable danger of fire. However much cooled, these gases at first carry away some of the most volatile of the tar-oils mechanically. Moreover they contain sulphuretted hydrogen, carbon bisulphide, perhaps carbon oxysulphide and other noxious gases, which may at times give rise to complaints of nuisauce. Towards the end of the process vapours of a very offensive and irritating kind are evolved, which are not completely condensed. Hence it will sometimes be necessary to subject the gases to a purifying process. An apparatus for this purpose, substantially as employed at a large London tar-works, is shown in figs. 70 and 71. The gas-pipes of all the cooling-worms are connected with a main pipe, which ultimately descends at *a* and enters the box *b c*. This is divided into two parts by a partition *d*, which does not reach quite to the bottom. The compartment *b* is empty, with the exception of a little water at the bottom, which is kept level with the lower edge of the partition *d* by means of the overflow pipe *e*. The compartment *c* is filled with coke or some other material presenting a large surface, and constantly moistened with water by means of the perforated cross *f*. This compartment serves as a scrubber: the gas is washed by the water; and at the same time the oily parts are condensed, owing to the slackening of the speed of the gases, the friction upon the surface of the coke, and the rinsing action of the water. It seems preferable to assist the division of the gas into many jets by nicking out the lower edge of the partition *d*, as shown in fig. 71. In most cases the gas will be allowed to escape by means of a pipe put on the top of *c*, either into the open air or into a chimney; only provision must be made for preventing the water in *b* from rising quite up to the partition *d*, so that the gas can pass through. But where it is desirable to prove to the public that no precaution against nuisance is neglected, a further purifying-apparatus is added, say an oxide-of-iron purifier *i k*, from which the gas escapes at *l* into a chimney-flue. This purifier is exactly like those used at the gas-works, but on a much smaller scale. If the washing in *c* is to be made especially good, the gas is forced right through the water by means of an injector *g*, which takes it through *h* to *i*. The liquid hydro-

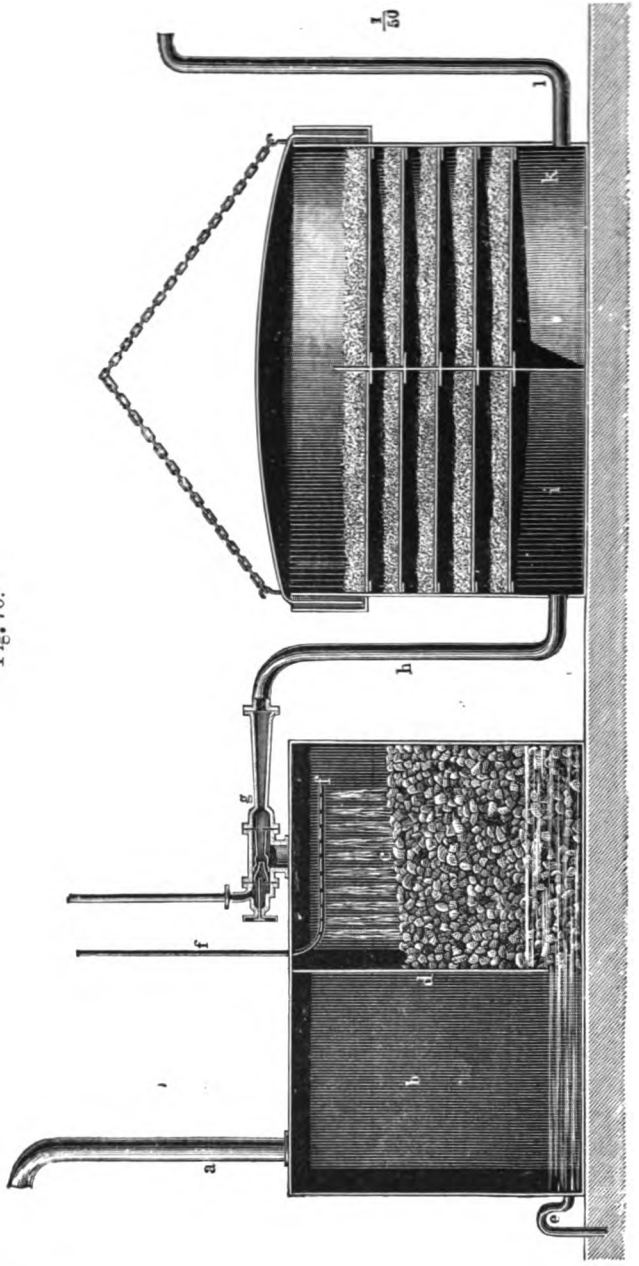
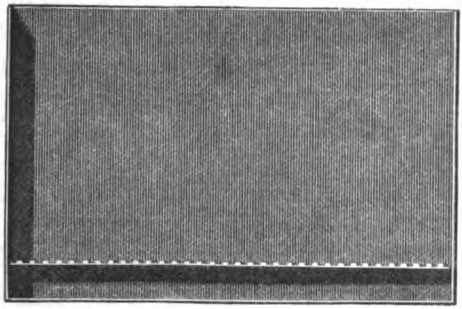


Fig. 70.

carbons are all retained in the vessel *b c*; the sulphuretted hydrogen is absorbed in the purifier *i k*; and the last remnant of the smelling gases is made innocuous in the hot fire-flue into which it passes through

Fig. 71.



Another arrangement for avoiding all nuisance, by the use of a vacuum, as devised by Mr. S. B. Boulton, will be described later on, when treating of the vacuum process.

Working of the Tar-stills.

The stills are charged with fresh tar while they are still hot from the last operation, but not so hot that they might suffer damage from the cold tar,—that is, a few hours after running off the pitch. The tar is either pumped in directly or run in from a higher tank previously filled. In both cases the bore of the feed-pipe is wide enough for the charging not to take too much time, say 6 inches; the air escapes not only through the condensing-worm, but also by an air-cock or by the overflow-cock *s*, fig. 58, p. 207. The latter also makes any other gauging of the contents of the still unnecessary. Where it is absent, the level of the tar must be ascertained by a float, or by a gauge-rod introduced into a hole, afterwards closed by a screw-plug. The stills may be filled up to the point where the cylindrical part merges into the dome-shaped one. Watson Smith states the permissible level at 9 to 12 inches below the man-hole—with thin tars, 18 inches below the same.

All the openings are now closed and the firing commenced. The heating-up may even be begun when the still is only half filled, as the level of the tar is then above the flues; although the air-cock or overflow-cock is then open, no loss is incurred, because

the heating-up of the large bulk of tar takes much time, and the new tar running in causes a constant cooling. Care must be taken to see that the worm is not choked up, which sometimes happens in this way: after the close of the previous operation the distillation slowly continues, whilst the water in the condensing-cistern cools down, so that "green grease" accumulates in the worm; this can usually be cleared out by blowing steam through the worm. As soon as the charge is all in the still and the openings are closed, the fire is increased; and this is continued up to the point at which distillation is about to commence. This will take more or less time, according to the size of the still and the season; with small stills (5-ton charge) it takes about two hours, with large ones (20- to 25-ton charge) it takes five hours in summer, six hours in winter. One or two hours after the commencement of firing, the tar begins to rise and froth; and now the greater part of the ammoniacal liquor can be run off by the overflow-cock. After this the firing must take place somewhat more cautiously, to avoid sudden boiling-over, which might otherwise take place with the violence of an explosion. From this time to the beginning of the distillation the fireman must always be in his place, and must watch the worm. As soon as the first drops appear at the end of the refrigerator, he must open the fire-door and slacken the fire; for now the danger of boiling-over is greatest. With proper management of the still this ought *never* to occur; but if it does take place, it is little use opening the fire-door, letting down the damper, &c., because the mass of heat stored up in the tar, the iron, and brickwork is too great; even completely drawing out the fire (which can only be done if the still is quite isolated) does not act instantaneously. But it does good to pour cold water onto the still-top; and the same means must be resorted to whenever for any reason the distillation is to be stopped as quickly as possible.

The following are signs that distillation is about to begin:— Vapours issue from the end of the cooling-pipe, often in puffs, and gradually drops are condensed from them. The still-head gets warm, and the worm also where it is not yet covered by the cooling-water. Now in any case the fire must be slackened; for the distillation will commence directly. This is still more necessary as soon as a continuous jet of liquid comes out of the worm; it is then time to open the fire-door, or, what is better, to let down the damper. If at this stage there is any excess of heating, the

ebullition takes place with violent bumping and frothing-up, and in the worst case the mass suddenly swells up and boils over. The tendency to eruptive ebullition is imparted to the tar by the water contained in it, and is all the greater the more water is present. It has been mentioned more than once how the quantity of water, and with it the bumping and frothing, can be diminished.

During the first period of the distillation permanent gases, water (containing ammonium compounds), and the most volatile tar-oils are given off, which always carry along some of the less volatile constituents, partly in consequence of the vapour-tension of the latter, partly mechanically. During this period the cooling-tank must be well supplied with cold water, both for condensing the tar-oils and because the condensation of the steam and ammonia liberates much heat. A 1-inch water-pipe and 15 feet head of water will supply a cooling-tank for a 20-ton still.

Almost everywhere the *first fraction* is that portion of the oils which comes over along with water; so that the first receiver contains both ammoniacal liquor and tar-oils. The latter are called first runnings, first light oils, crude naphtha, &c. Water will form a greater or smaller proportion of the distillate, according to whether it has been previously removed or not; this proportion is ascertained by catching some of the distillate in a glass cylinder, in which naphtha and water separate at once, the former floating on the top of the water. At first much water and little oil comes, then less water and more oil; sometimes the time when the water ceases to come over can be fixed pretty sharply for changing the receiver. But it is safer to wait till the distillation slackens. This is called the "break," and is probably caused by the fact that the aqueous vapour carries along a quantity of oils of much higher boiling-point than that of water; so that, after all, the water is removed first. The temperature has to rise a good deal before the liquid begins to boil anew. At this stage sometimes for two hours hardly any thing comes over but a little water; and, from the peculiar noise made by the steam within the still, this period is sometimes called the "rattles." The cause of the rattles is the falling-back into the contents of the still of the last portions of water which had been vaporized and had been condensed before getting into the worm. When coming in contact with the tar, now heated considerably over 100°, it is instantaneously re-vaporized with a somewhat explosive force, and thus the rattling or crackling

sound is produced. The same thing is often observed when distilling, in the laboratory, naphtha containing traces of moisture. The rattling noise ceases when the temperature has risen high enough; and the distillate then comes over in a thick, quiet stream. It is now mostly collected in another receiver as "light oil," or "second light oils."

The ceasing of the appearance of water is not by itself a sufficient signal for changing the receiver; for sometimes a little water comes off along with the light oil, and even, at first, with the heavy oil, from the hydration water of phenol. Hence other signals must be the smell, the specific gravity, and the quantity of the distillate, or else the indications of the thermometer. The smell, which of course cannot be very well defined, generally shows the attendant quite clearly when he must change the receiver for light oil: the first runnings smell much more pungent than the light oil; and the transition is pretty sharp. The specific gravity increases slowly, and does not in this case give very distinct guidance.

If the fractions are to be made according to the indications of the thermometer fixed in the still (p. 212), it is usual to change at the following points:—

1. First runnings, up to 105° or 110° C.
2. Light oil, up to 210°.
3. Carbolic oil (for phenol and naphthalene), up to 240°.
4. Creosote oil, up to 270°.
5. Anthracene oil, above that.

These points are, of course, not always the same, partly because the thermometers do not reach down exactly to the same depth. Thus a large German works changes as follows:—

1. Light oils, up to 165° or 170°.
2. Middle oils (for carbolic acid and naphthalene), up to 230°.
3. Creosote oil, up to 270°.
4. Anthracene oil, above that.

Girard and DeLaire (*loc. cit.* p. 10) quote the following fractions:—

1. Huiles légères, from 30–140°, sp. gr. 0·780–0·850.
2. Huiles moyennes, „ 150–210°, „ 0·830–0·890.
3. Huiles lourdes, „ 220–350°, „ 0·920–0·930.

(The specific gravities are evidently wrong, and, no doubt, again prove an unaccountable confusion with paraffin oils.)

In the case of tars of known quality, the time and the quantity of the distillate are among the most important signals for changing the receivers. The former varies of course with the size and even with the shape of the still, its setting, &c. We shall make some statements on this point and on the quantity of the different fractions at the end of this chapter. The quantity of the distillate can only serve as a guide where each still has its own receivers, which is rarely the case at large works.

Attempts have been made to greatly increase the number of fractions at the first distillation of coal-tar, with the view of better isolating the products therefrom. All such attempts have failed hitherto, and probably will continue to do so in future. In no case are pure products obtained; and hardly any of the subsequent rectifications are saved; so that the whole is but a superfluous complication of the process. This is founded on *the nature of fractional distillation*, which has only recently been cleared up by a number of researches*.

The various components of a mixture do not distil simply in the order of their boiling-points, not even taking into account the vapour-tension of the substances not yet arrived at their boiling-point; but their vapour-density must also be taken into account. According to Dossios and Wanklyn, the quantity of each component distilling at a certain temperature is found by multiplying its vapour-tension at the boiling-point of the mixture into its vapour-density, or, what comes to the same thing, its molecular weight. Thus methylic alcohol (molecular weight=32) boils at 66°, methylic iodide (molec. weight=142) at 72°; but from a mixture of the two, more of the latter distils over. A mixture of 91 parts carbon bisulphide (boiling-point 47°) and 9 parts alcohol (boiling-point 78°) boils constantly at 43–44°, and during distillation retains its composition. Hence the liquid possessing the highest vapour-tension does not necessarily distil most rapidly; for what its companions lack in tension they may make up in vapour-density. If the tension is called t, the vapour-density d, we have for different liquids $x=ktd$, in which formula k is a constant to be found by experiment in each single case. If the vapour-

* Dossios, Jahresb. f. Chem. 1867, p. 92; Wanklyn, Philos. Mag. (4) xlv. p. 129; Glashan, ibid. p. 273; Naumann (comp. below); Thorpe, Journ. Chem. Soc. 1879, xxxv. p. 544; F. D. Brown, ibid. p. 547; 1881, xxxix. p. 304; Konovalow, Ber. d. chem. Ges. 1881, pp. 2224 & 2678, &c.

densities and tensions are inversely proportional to each other, and the values of k are equal, the products $k_n t_n d_n$ will all be the same; *i. e.* the mixture will remain unchanged throughout the distillation. For this reason homologous series (*i. e.* those whose members differ from each other by CH_2) are not easily separated by fractionating; for whilst the vapour-tension is lowered by each CH_2, the vapour-density rises. This explains why so many substances distil more quickly in a current of steam; for aqueous vapour is one of the lightest bodies. By diminishing the pressure the difference between the vapour-tensions of different liquids is increased, whilst their vapour-densities remain the same*; hence they are more easily separated, as is proved by the success of exhaustion in gas-making and tar-distilling (see below).

A mixture of two liquids which are not mutually soluble, on distillation exhibits a boiling-point below that of the more volatile substance. A mixture of carbon bisulphide (boiling-point 47°) and water boils at 43° &c. This observation has been generalized by Naumann†, who found that the boiling-point of such a mixture is constantly below that of the most volatile component,—and also that the proportion of substance is always the same, viz. equal to the proportion of the vapour-tensions of the two components, measured at the temperature of boiling, multiplied by their molecular weight. This behaviour is of importance to us in tar-distilling also, where water boils along with oils not miscible with it. Thus, although at 98° the vapour-tension of naphthalene is only 20 millim., that of water 712 millim., yet at that temperature 49·4 grams of water pass over with 8·9 grams of naphthalene.

It is hardly necessary to mention that the different fractions are not divided by any sharp lines, and that at different works they are taken differently. In some places no distinction is made between first runnings and light oils, but all that has a specific gravity below 1·0 is taken as crude naphtha. The subsequent treatment must be adapted to this.

In any case *first runnings* and (aqueous) *ammoniacal liquor* come together, the former floating on the latter. The latter is worked up like any other similar liquor, as will be described in the last chapter. The two liquids at once separate sharply; the water is either pumped away from below, or is continuously carried away

* Winkelmann, Poggend. Annal. N. F. i. p. 430.

† Ber. deutsch. chem. Ges. 1877, p. 1421; 1879, pp. 2014, 2099.

by a pipe starting from the bottom of the receiver and turned upwards; or else the same object is obtained by a partition reaching nearly to the bottom of the receiver, or in any other way.

Light Oil (Second Runnings).

The *second fraction* (if the distillate coming over before the carbolic oil is, as usual, divided into two fractions) begins after the "break," when the distillation proceeds quite smoothly, in a full stream and without any further danger of boiling over. The product is no longer a naphtha, but has a more oily nature; it is called either "light oil" or else "second light oil," or "second runnings." We shall in future use the former name in this restricted sense. This fraction is usually continued up to the point where its specific gravity is equal to that of water. The men run a few drops into a cylinder partly filled with water; if the oil floats anywhere within the water in single, large, globular drops, its specific gravity is $=1{\cdot}0$, and it is now time to change the receiver for carbolic oil. Where the fractions are made by the thermometer, this point will be at about 210°. This proves that the light oil must contain a good deal of carbolic acid (b.-p. 180°) and naphthalene (b.-p. 218°); but it must be remembered that in the upper part of the still and in the still-head some cooling takes place and the vapours partly condense again; hence the principal part, especially of naphthalene, only comes with the next fraction. But where carbolic acid and naphthalene are principal considerations, the fractionation is managed accordingly. This is the object of the style of working mentioned on p. 228, where the "middle oil," passing over between 165° or 170° and 230° will comprise nearly all the phenol and naphthalene, especially if the bulb of the thermometer is not placed in the tar, but in the liquid.

Another signal, sometimes used, for changing from light oil to the next fraction is obtained by letting a few drops of the distillate fall upon a cold piece of iron. If a crystallization of naphthalene sets in, it is time for changing. But this only holds good where no "carbolic oil" is separately received.

During the time the light oil is coming over (that is, after the break), the fire is increased without any danger of boiling over, although even now for the most part a little water appears, probably owing to the hydrate of phenol splitting up. Now the cooling-water begins to get warm; but little or no fresh water is

run in; so that at the end of this stage the temperature of the water surrounding the worm is about 40°. If the work is arranged for "middle oil" in the above-mentioned sense, the water must be at least from 50° to 60°. Afterwards no fresh water at all must be run in; and sometimes even steam must be blown into the cooling-tank by means of a pipe entering at its *bottom* and pierced with numerous holes (*b*, fig. 62, p. 216): this is necessary because the danger of the worm being choked up is greatest in the bottom coils. Such a danger sets in even more near the end of the process, as we shall see afterwards; but it can be always provided against by allowing the water to get hot. Some English tar-distillers have not even steam-pipes in their refrigerators; but this is advisable in any case.

If the temperature in the refrigerator were kept too low, in the later period of the light-oil stage the naphthalene would crystallize and choke up the worm, thus producing a dangerous pressure in the still. The explosions of tar-stills, rare as they are, are probably always caused by neglect in this respect, either during the naphthalene- or the anthracene-period *. On the other hand, the water should not be allowed to get warm at the beginning of the light-oil stage, because then considerable quantities of the more volatile hydrocarbons are still coming over. This seems to be another reason for continuing the first fraction till benzene and all its homologues have passed over, and then condensing the "middle oil" with warm cooling-water.

Whether the worm is choked up, or not, is best seen at the end of the pipe coming out of the refrigerator, where it is curved up to allow the permanent gases to be taken away. This pipe should be warm; and the liquid should run out uninterruptedly: this is readily seen when it runs into a glass jar (*c*, fig. 68, p. 220). Where there is an intermediate vessel (*e*, fig. 68) with cocks for the different fractions, the distillate might possibly crystallize in this, or in the pipes *g g* that carry away the products. This is not so very dangerous, because the whole box *e* must be first filled with crystals before the worm can be choked up; notice will be given of it by the box *e* or the cocks *f* getting cold. If the pipes *h* are sunk in the ground, if they are covered up, if they have sufficient fall and are not too long, they will not be easily stopped up; but it is

* A frightful explosion occurred in this way at a tar-works near Gateshead-on-Tyne, in 1886, by which several people were killed, among them the managing partner. The tar-stills were not provided with safety-valves.

decidedly advisable to be prepared for that contingency by making provision for blowing steam through them.

Where the work is carried on with evacuation by an air-pump or an injector, in the manner to be described hereafter, there is absolutely no danger of any choking-up of the worm. But in any case the stills ought to be provided with a safety-valve or an equivalent contrivance (p. 211).

J. Vaughan* proposes preventing explosions that might occur in consequence of the worm choking-up, by means of a wide pipe reaching nearly to the bottom and passing out at the top connected with a large empty cylindrical boiler placed near the still and at a lower level. The connecting-pipe is enlarged at the highest point, and at this place is closed by a valve kept down by its own weight. The whole of the pipe is kept warm. If any excessive tension should occur within the still, the tar will rise in the pipe, lift the valve, and flow over into the empty cylinder. This is evidently exactly the same thing as that practised in Germany many years ago (p. 211).

Carbolic Oil.

The distillate at and above the specific gravity 1·0 was formerly not fractionated at all, but collected all together as heavy oil, dead oil, or creosote oil, and sold for pickling timber, without any further manipulation. Only exceptionally could the first and the last portion of the creosote oil be separately sold, the former for carbolic acid, the latter for lubricating-grease. When carbolic acid was aimed at, there was but rarely a special fraction made for it; the light oil was only driven a little further. No doubt phenol and its homologues, as we shall see in the 9th Chapter, occur also further on in the heavy oil, and constitute part of its value for preserving wood; but making pure phenol from proper heavy oil is rather difficult and expensive, and only takes place exceptionally. For this reason, since large quantities of phenol have been required for the manufacture of colours, for disinfecting, and for medicinal purposes, it has become usual to make a special fraction containing as much carbolic acid as possible and with it a great deal of naphthalene. Although the boiling-points of these compounds are wide apart (180° and 218°), a large quantity of naphthalene is carried over below its boiling-point, and, on the other hand, phenol is kept back in the tar-oils above its boiling-

* Engineer, 1880, v. p. 298.

point. Where no thermometer is placed in the tar-stills, this fraction is made to commence whenever the specific gravity of the distillate is 1·0; moreover its yellower colour and its smell serve as guides. A certain quantity of the oil now passing over is received as "carbolic oil;" and when this quantity has come over, the change for creosote oil is made. The amount of carbolic oil is usually 100 gallons from a charge of 2000 to 2500 gallons, *i. e.* 4 or 5 per cent. of the tar. Ordinary Lancashire tar yields 5 per cent. by volume of good crude phenols, yielding 65 per cent. (by volume) of a carbolic acid, sufficiently pure to crystallize at ordinary temperatures with ease (Watson Smith, Journ. Chem. Soc. 1886, vol. xlix. p. 21).

In Germany it is usual (as it is more rational) to consult the thermometer. We have already mentioned that at some works the fraction passing over between 210° and 240° was taken as carbolic oil (probably the bulb of the thermometer dipped in the liquid itself), whilst at another (very large and well conducted) works the "middle oil" was received between 170° and 230°. The latter course seems most worthy of being recommended, as it leaves a suitable margin below the boiling-point of phenol and above that of naphthalene.

If the oils on cooling show a large crystallization of naphthalene, this is a sign that most of the phenol has already come before, or that it is now time to change for creosote oil; for naphthalene is much more soluble in phenols than in the heavy indifferent tar-oils, and hence mostly remains dissolved in the distillate as long as there are considerable quantities of phenols present, but crystallizes in large masses on cooling when the phenols are becoming scanty; but this rule is not without exceptions.

Each factory must, of course, find out for itself which are the proper limits of this fraction: they will depend upon the size and contents of the stills, the position of the thermometer, the quantity of the tar, &c. The criterion is that the crude carbolic acid, obtained by the subsequent treatment of the carbolic oil, is of the proper quality, as will be explained in the 9th Chapter. As far as naphthalene is concerned, enough of it is sure to come over, and sometimes it crystallizes out in large quantities. Only exceptionally does tar contain so little naphthalene that it is not partly separated in the solid state. Hence the previously-mentioned precautions for preventing the choking-up of the pipes should be always observed in this case.

Creosote Oil.

The fraction which comes over after the carbolic oil generally contains at first sufficient naphthalene for some of it to crystallize on cooling in a shallow dish. But after some time this ceases; the naphthalene, still present, but in smaller quantity, remains dissolved in the liquid hydrocarbons even after cooling; and as phenol and its homologues, which impart to the products the property of promoting friction, have ceased even before, the portions now received possess a milder, more oily or greasy nature, which makes them suitable for cart-grease. Hence this product is sometimes called "soft oil," or "liquid creosote oil." It generally begins to appear when about half of the heavy oil (calculating for a distillation up to hard pitch) has been received. Before an industrial use had been found for the anthracene oil, sometimes the second half of the heavy oil, *i. e.* the "soft oil," along with the "red oil" or anthracene oil, was run into a special receiver as "grease oil," sometimes the liquid soft oil was separated from the butter-like grease. This was done chiefly in the first years after 1860, when, owing to the American civil war, the price of rosin had risen enormously, and the cart-grease-makers were glad to get any substitutes for rosin-oil; and this is now again done at some tar-works. The liquid soft oil is sometimes called "yellow creosote," from its yellowish-green colour, which soon, however, changes into dark brown. Its value as a lubricant is inferior to that of the last portion, the "solid creosote" or a green grease answering to the present anthracene oil. In any case these products are very much inferior as lubricants to rosin-oil or lubricating oils from petroleum and paraffin-oil refineries. The separation of yellow from solid creosote is now principally made for the purpose of obtaining, in the "*anthracene oil*," that constituent of coal-tar (viz. anthracene) which, since Graebe and Liebermann's discovery of artificial alizarin (1868), has become far the most valuable product of this industry. All the remaining heavy oils are put to the uses to be described in the 8th Chapter.

Since the tar made at the Scotch gas-works contains too little carbolic acid and anthracene to make it worth separating, most of the Scotch tar-distillers do not make the fraction here described, but collect all the heavy oils together for the pickling of timber.

Anthracene Oil.

The beginning of the anthracene-oil period is either judged by outward marks or by the thermometer, sometimes by the quantity of the distillate. Usually it is calculated that about one sixth of the heavy oil (reckoning from sp. gr. 1·0 up to hard pitch) comes over as anthracene oil; but in some cases as much as one half of the heavy oils is collected as anthracene oil. The latter may be reckoned to begin when the oil ceases to remain liquid after complete cooling—that is, when a fresh separation of solids sets in. Where the thermometer is employed, 270° is nearly everywhere assumed as the commencing-point. Probably this general consent results from the fact that from this stage the thermometer-bulb is universally in the vapour. Sometimes first and second "green oil" or "red oil" are received separately.

End of the Distillation.

Formerly this was decided according to whether hard or soft pitch was to be left in the still. Sometimes, but rarely, the work was stopped as soon as all the light oil had passed over; the residue then remaining in the still was called "asphalt," and employed in the paving of streets, for protecting underground iron tanks from corrosion, and similar purposes (see next chapter). But the work was nearly always continued further, either up to soft pitch or hard pitch (*brai gras* and *brai sec*). Soft pitch is obtained when only half the dead oil is distilled off—that is, just as the "soft oil" is coming; moderately hard pitch, when the soft oil and the first portions of anthracene oil are taken away; hard pitch, when the distillation is carried to its conclusion, as will be described presently. The special characters of these different descriptions of pitch will be given in the next chapter.

Since anthracene has become the most valuable product of tar-distillation, wherever the tar is not very poor in anthracene (comp. p. 235) the distillation is mostly continued till hard pitch is produced. In England and France it is frequently run out in this state; but in many English and Scotch works, and in most or all German ones, they manage differently, as we shall see.

In the last period of the distillation the water-supply to the worm-tub must be shut off altogether, and the water in the tub

must be allowed to boil; if necessary, ebullition must be produced by blowing in steam.

The distillate which now separates is a mixture of anthracene, phenanthrene, carbazol, &c.; later on also of chrysene, pyrene, &c.; and ultimately contains so much of these that on cooling it solidifies in a butter-like mass which would choke up all the pipes. This must of course be avoided by keeping the worm-tub and the conveying-pipes warm, or even (more safely) by employing steam; but the best way of all is by producing a vacuum (see below). The oil running off should be about 60° C. If the distillation is continued till hard pitch is formed (*i. e.* pitch which will be hard when cold), it becomes at last very sluggish; its cessation is determined by the manner in which the distillate solidifies, and by its quantity—also by the time elapsed, and by the peculiar smell, now again changing. Steam being usually injected now, the thermometer is of no further use; and in any case a mercurial thermometer could not be employed at this stage, the temperature in the interior of the still being about 400°. In the case of tars containing too little anthracene, &c., to solidify, the other signs must suffice for judging when to stop. Frequently, also, the hydrometer is consulted. If the distillate shows a specific gravity =1·080–1·090, the residue will be moderately hard pitch; at 1·120 it will be hard pitch; but this does not hold good of all descriptions of coal-tar, and should be tested by experiment. As soon as the distillate assumes a "gummy" state, the distillation should be stopped, for this product, although still containing anthracene, cannot be filtered at all.

If the distillation is continued too long, much damage is done in more ways than one. In the first place, the anthracene is too much contaminated with chrysene and pyrene; again, the pitch is half coked: in the worst case it ceases to run out of the still; and even if it does run, it does not solidify in a glass-like, but in a porous, honeycombed form, and is quite unsaleable. Lastly, the still itself is much damaged by this treatment.

E. Kopp* proposed driving off only a portion of the creosote oil and *distilling the soft pitch to hard pitch in a special still.* He asserted that he had found in such soft pitch from the Turin gas-works 4 to 6 per cent. anthracene; but this seems very improbable, and it should be remembered that at that time no exact

* Bolley-Kopp's 'Spinnfasern,' p. 381.

methods for estimating anthracene were in existence. The pitch-still was to have a greater width than depth; the gas-pipe was to be of large bore, to join the still only 6 or 8 inches above the level of the boiling pitch, and then to bend down at once, in order to carry away more readily the heavy vapours. Towards the end the distillation was to be promoted by a current of superheated steam, or of heated air which had been passed through a red-hot pipe filled with charcoal, and thus converted into a mixture of carbon monoxide and nitrogen. During the distillation as much melted pitch as corresponded to the oil distilled was to be run into the still by means of a pipe reaching through the still-cover halfway down into the pitch; this would amount to half as much as the original charge of pitch in the still. The steam or heated gas was to issue either immediately above the surface of the boiling pitch or within the same. Lastly, when the contents of the still had become too thick they were to be expelled by the steam or air, the cooling-worm having first been shut off. We do not know whether Kopp's proposal has ever been carried out in practice. That part of it which refers to promoting the distillation by a current of steam or gas has been proposed and carried out elsewhere (see below). There remains the proposal to effect the distillation to hard pitch not in the same still from beginning to end, but transferring the last stage to a separate vessel. This would not be very easy to do, and would not pay unless more anthracene were got out, which has not proved to be the case.

We must distinguish between this distillation of soft pitch up to the stage of hard pitch, and that of hard pitch itself to coke, which will be described in the next chapter.

Employment of Steam in the last Stage of the Process.

Apart from what would happen if hard pitch were run off too soon, the still-bottom naturally suffers considerably during the last stage of the process, when the heat has risen to a high point, especially where it is not protected by a curtain arch. At the same time the vapours now formed, which are very heavy, cannot so easily get out of the still into the worm, the level of the mass being now very low, and the upper part of the still not being heated; a portion of these vapours must condense again within

the still itself; and the distillation is but sluggish. The longer it lasts, the more opportunity there is for the hydrocarbons to split up into carbon and permanent gases. Hence it seems rational to promote the carrying-away of the vapours at this stage, either by superheated steam &c., or by by a vacuum, or both.

Steam seems to have been employed for a long time past to promote the distillation, not merely at the commencement, as described, p. 192 *et seq.*, but again in the last stage, when it must, of course, be first superheated.

It is, for instance, mentioned in Cormack's patent, No. 1368, June 2, 1864. According to Watson Smith, Mr. John Barrow, in Manchester, employed steam as a secret process about the same date. I am informed by Mr. S. B. Boulton that the introduction of steam is fully described by Dr. Gesner in a work upon "Coal, Petroleum and other distilled Oils," published in London, Paris, and New York, 1865; also that Mr. Boulton experimented with steam in 1865 and 1866, in conjunction with M. Audouin, and that he has used it for many years past. Steam is also mentioned in Audouin's patent of 1872 (see next page), but only as a means of stirring up the contents of the still. The use of steam, however, did not become general until recently. At the present time every well-appointed tar-works possesses tar-stills provided with steam; and by that means most of the troubles formerly caused by quickly destroyed bottoms, by explosions, &c. have vanished.

The steam fulfils more purposes than one. It assists in carrying away the vapours as before mentioned; this shortens the time required for the distillation and increases the yield: besides, it prevents the pipes from being choked up. Thirdly, the formation of hard crusts upon the still-bottom is lessened by the temperature just at that place being kept comparatively low, and also by the agitation of all the contents of the still, so that coking and burning-on of the pitch cannot easily take place. Indeed, Trewby and Fenner assert that with their system, shown in figs. 58 and 60 (pp. 207 and 208), no coke at all is formed on the still-bottoms, and thus cleaning-out the still becomes unnecessary. At all events, the Beckton stills go for many months without cleaning. Elsewhere experience has not been quite so favourable, perhaps because the steam was introduced by a simple cross of tubes, &c.; whilst by Trewby and Fenner's plan steam ranges over every part of the still-

bottom, issuing from numerous and suitably-formed outlets. For this reason we have adopted their system (introduced at the great Beckton works) in our diagrams, without undertaking any responsibility if it should be found too complicated and the outlets too liable to be choked up. Of course any similar arrangement will answer the same purpose. The arrangement described (but not figured) in Audouin's patent of 1872 already consisted in projecting jets (of carbonic acid, combustion-gases, steam, and the like) in all directions, preferably downwards, and near to the bottom and sides of the distilling-apparatus.

The pressure of steam employed in tar-stills usually ranges from 3 to 5 atmospheres.

A further question is, In what way is the steam to be superheated? At a German works the superheater is a coil of ¾-inch wrought-iron tubing, with a bottom surface of 3 feet 3 inches square, placed in an oven-like space above the fire-arch. The boiler-steam is first freed from liquid water in a suitable catch-pot, and then enters the superheater, where it attains a temperature of 275° C. The steam-pipe, where it issues again, is covered with a thick non-conducting coating, and runs over the top of the still (which has the shape of a steam-boiler), into which it sends four branches. Each of these is provided with its own cock, and also with a special air-cock, through which the steam is blown off for a moment in order to remove any condensed water, before the cock leading into the still is opened. This arrangement has been in operation ever since 1873, and gives perfect satisfaction. The steam is first blown in when the change is made for anthracene oil—that is, when the thermometer has got up to 270°. From this time to the end of the process no more firing takes place; the heat stored up in the arch that runs all along the still-bottom, together with the superheated steam, suffice to finish the distillation. After the anthracene oil has been got out, creosote oil is pumped into the still, to make soft pitch or "prepared tar" (compare Chapter VI.), which lowers the temperature so far that the still can be emptied at once and recharged.

A similar system of completely dried and then superheated steam I found at another German works, employed with stills of the usual cylindrical form with concave bottom, and giving complete satisfaction.

Some English manufacturers do not superheat the steam at all,

as they find that in their system, where it is conducted through the tar in so many fine jets, it is by this alone superheated to the temperature of the tar. But I have observed also at a German works, where the steam was simply introduced by a cross of tubes, that no special superheating took place, the superheater formerly employed having been dispensed with. But the steam was previously dried, and caution was always used in first starting it, as any water carried into the still would cause an explosion when suddenly brought into contact with tar standing at a temperature of 300° and above. This has actually taken place at more works than one. Just for that reason we would advise in any case such a slight previous superheating as will *completely* dry the steam, which can be done without any expense whatever.

The employment of dry steam at the end of the process has the further advantage that in running off the pitch no air need be admitted into the still, which otherwise might lead to explosions or fire.

Cabot (Amer. Pat. No. 184,182) seeks to promote the distillation of anthracene by blowing *petroleum* into the mass—a process of very doubtful value.

Mechanical Agitators in Tar-stills.

Sometimes mechanical agitators are employed in tar-stills in order to avoid superheating the bottom at the end of the process. Such apparatus is mentioned in several patents, as Lennard's, Berninghaus', and Fenner's (pp. 206 & 213). Mechanical agitators are also mentioned in Audouin's patent (No. 1456, of 1872), along with agitation by means of a stream of illuminating-gas, carbon dioxide, air, smoke-gases, or steam. It is asserted that in this way 10 to 15 per cent. more anthracene is got than usual.

Mechanical agitators are especially found useful when distilling tar very rich in fixed carbon (coal-dust mechanically suspended), which sometimes occurs in large quantities, and in distilling the tar causes the formation of hard crusts of coke at the bottom of the still. This is prevented either by injecting superheated steam, as before mentioned, or by a mechanical agitator, consisting of a revolving shaft with chains dragging along the bottom. In one trial with this apparatus, after fifteen distillations the still-bottom was found to be almost quite clean, and much less coal had been used

for firing. The rivet-heads, as well as the links of the chain, were certainly ground off, and it was found necessary to renew the chain and to re-rivet the still-bottom after six months, but the

Fig. 72.

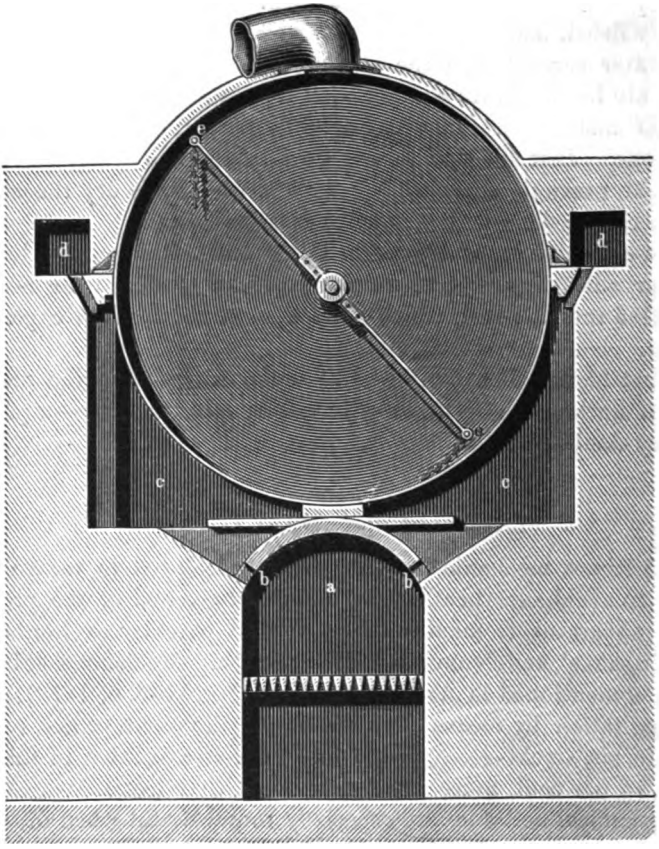
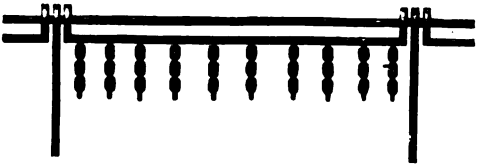


Fig. 73.



latter could be avoided by countersinking the rivets. There was no deformation of the still-bottom. In this way it became possible to distil such tars down to hard pitch, which was softened again by the addition of dead oil*.

It does not seem necessary to employ agitators in the case of ordinary tars. At Beckton, where Fenner's agitators had been introduced in some of the stills, Mr. Wilton found no advantage against the system of simply blowing in steam during the latter part of the distillation, and the use of the agitators was therefore discontinued.

At some Scotch works mechanical agitation is employed not during the distillation itself, but at the end, when heavy oil is run in for the purpose of softening the pitch. This is done at Dalmarnock, Glasgow (Messrs. George Millar & Co.). Figs. 72 & 73 show the stills there used, as described in Dr. Ballard's Report to the Local Government Board for 1878 and 1879, p. 139. Several stills, in the shape of horizontal iron cylinders, 21 feet long and 8 feet 6 inches diameter, are placed side by side in a set. The heat from the fire *a* does not impinge directly upon the bottom of the still, the fireplace being arched over along its whole length (compare p. 203). The fire-gases pass through twenty openings, *b b*, on each side of the arch into the flue *c c*, and thence through similar openings into the flue *d d*, leading to the chimney. The still-bottom touches the arch, but does not rest upon it, the still being suspended by stout angle-irons from the side masonry. In order to keep the inside of the still-bottom clean, horizontal bars *e e*, shown in elevation in fig. 73, reaching to within 3 inches of the shell of the cylinder, are made to revolve round and round. To these bars are attached, at intervals of a few inches, short pieces of iron chain which drag along the bottom and prevent deposition. The chains are arranged upon the bars in such a manner that those of the one bar scrape the cylinder-bottom in the places in which it is not scraped by those of the other bar. This apparatus lasts for many years without repairs.

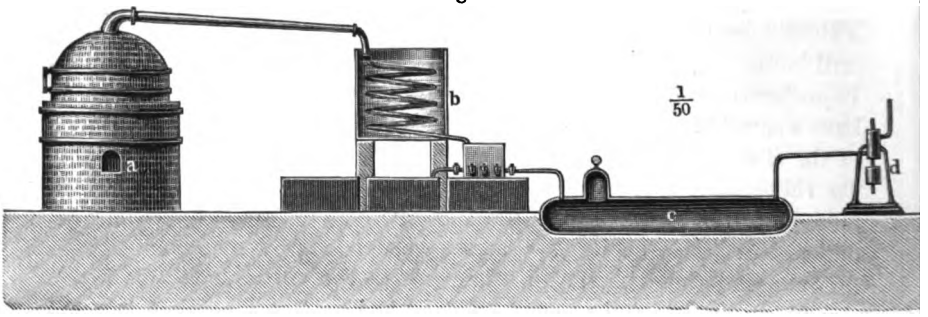
Employment of a Vacuum.

Excellent success is claimed for the *employment of a vacuum*, which I saw in operation at a German works in the year 1880

* Wagner-Fischer's Jahresbericht for 1885, p. 464.

in the following manner. The distillation is commenced at the ordinary pressure, and continued till it is time to change for anthracene oil. Now a steam-pump is started, which aspirates both gases and oils away from the condensing-worm into a large boiler sunk in the ground, where the anthracene oil remains whilst the gas is forced out by the pump. From the same pipe steam is injected into the still, as above described, but merely to keep its bottom clear; for no choking-up ever happens, even without the steam: the pump sucks away the butter-like mass quite easily into the boiler. The vacuum-gauge in this showed 15 millimetres mercurial pressure. On their way along this boiler the products were cooled, so that the gas coming out of the far end entered the pump nearly cold. When the distillation was finished, the same boiler served as a pressure-apparatus for forcing the oils into the anthracene-crystallizers. The whole arrangement answered so well, that a second apparatus of the same kind had been mounted for creosote oil; but this had not yet started at the time of the author's visit. The greatest advantage of this plan is the regularity of working, and the complete absence of any danger of choking up the pipes. An injector had been tried in lieu of the steam-pump, but had not answered so well. The sketch (fig. 74)

Fig. 74.



may serve for elucidating the process. In this, *a* is the tar-still, *b* the condensing-worm, *c* the anthracene-oil-boiler with its dome, vacuum-gauge, steam-pipe, &c.; *d* the air-pump.

The first introduction of the vacuum in tar-distilling seems to be due to Mr. S. B. Boulton, who applied it in more widely extended ways than that just described, and in such a manner as to

prevent all nuisance. The following description of his arrangement is taken from Dr. Ballard's Report to the Local Government Board for 1878 and 1879, p. 142:—"But the most perfect arrangements for preventing nuisance from uncondensed and non-condensable vapours and gases that I have seen are at Messrs. Burt, Boulton and Haywood's works at Silvertown, near the Victoria Docks. From each condenser the condensed and uncondensed matters pass into a receiver having an opening at the top, which is firmly closed down, during working, with an accurately-faced iron cover. Out of this receiver the condensed liquids are drawn off below to the store-tanks, while the uncondensed gases and vapours are drawn off above by an air-pump or gas-exhauster, worked by a small steam-engine provided for the purpose. These gases and vapours from all the whole row of receivers pass into an exhaust-main, which communicates with two 'washers'—the first arranged like a chemist's Woulffe's bottle. They have to pass through both of these, where a certain amount of further condensation takes place. They then pass through the exhauster to a third condenser or 'washer,' shaped like a boiler; and here again they have to pass through water and over water for some feet to the discharge pipe, which conducts such as are still uncondensed to a fire, where they are consumed. This exhausting arrangement has the further value of assisting to draw off the products of distillation from the still, and to clear this of offensive gases which would otherwise escape into the air during the process of recharging with tar. Another advantage which these manufacturers say they thus obtain is that the watery vapours (containing sulphide of ammonium) which accompany the naphtha and benzol series of products, and which were formerly wasted, are now collected and utilized for the manufacture of sulphate of ammonia. The benzols also themselves are increased in bulk from the greater care with which these lighter vapours can be collected. Further, by the use of the air-pump and the closed receiver, the duration of the whole distilling operation is abridged very sensibly, which is itself a source of great economy in a large manufactory."

A somewhat complicated apparatus for distillation (of alcoholic liquors) in a vacuum has been constructed by N. Galland (G. P. 17972, 1881).

Running-off the Pitch.

When working in the old manner (*i. e.* without steam &c.), it is necessary to fire up to the end, and that sharply. As soon as it is considered that the operation is at an end, the fire-door is opened, the coals are drawn out, and soon the distillation ceases. But the pitch cannot be run off at once, partly because there is danger of its taking fire, and partly because the large amount of heat stored up in the still and the brickwork might damage the still. Hence some time must elapse before the pitch can be run off with the precautions prescribed above—two, six, or even twelve hours, or even longer, according to the size of the still. After the pitch has been let out, again some hours must pass before coal-tar is pumped into the hot still, lest the sudden contraction on cooling should start the rivets &c. At first sight it would seem most suitable to wait rather longer before letting out the pitch, and thus further to diminish the danger of its taking fire; but it is much more important that the pitch should be perfectly liquid when run off, so as to leave the still completely empty. The outlet-cock must be arranged with the same view. Whatever pitch remains in the still is changed by the heat retained by the brickwork into coke, which covers the still-bottom as a non-conducting layer, does not dissolve in the fresh tar, and would soon cause the bottom to be burnt away, if it were not from time to time knocked off and cleaned out like boiler-scales. With ordinary English stills, this must be done after three or four distillations; but proper placing of the cock, protecting the bottom by a curtain arch, and twelve hours waiting will prolong the time to about a month.

The treatment of the stills, as regards running off the pitch, is very much facilitated by the use of steam during the last process, and this is not one of the least reasons for introducing the steam treatment. But the operation is very much simpler if *the pitch is softened in the retort* before running off. In this case the distillation is, in the first instance, carried on so far that the residue, if it were run out and allowed to solidify, would yield "hard pitch." This is, however, not done, but creosote oil or the oils draining from anthracene (see Chapter VII.) are pumped back into the still containing the liquid pitch, and thus mixtures are produced of any degree of viscidity, or even liquid at the ordinary temperature, the latter being sold as "prepared tar" or "refined

tar." The mixture of the liquid pitch and the oils pumped into it takes place without any special appliance, but it is, of course, promoted by mechanical agitation, for which purpose the Scotch stills, shown in figs. 72 and 73 (p. 242), have been especially constructed.

Where the pitch is softened in the stills themselves no choking-up of the outlet-cock or taking fire of the pitch in the air on running off need be feared; and crusts of coke on the still-bottom would probably not appear to any great extent, even if steam were not applied, as is now almost universally done.

An outlet-cock can be dispensed with altogether if the soft pitch, after some cooling, is forced out by means of perfectly dry steam or of a vacuum through an upright pipe that comes out of the still-top and conveys the pitch to some safe place. The outlet-pipe should start from the bottom of the still (which in this case may even be convex), and rise perpendicularly to the highest point, and thence descend in a gentle curve; it must be heated up by steam before the forcing begins. There is in this case no danger of any fire in the pitch-cooler; and the process has answered very well indeed at several works (compare the sketch p. 215).

At some Scotch works the soft pitch is pumped out from the top of the still, without any exposure to the air, through a close iron conduit, to the pug-mill, in which it has to be manufactured into "asphalt." If this conduit be sufficiently inclined, no cleansing of it will ever be required.

Running-off the *soft* pitch (which is not so very hot, does not take fire in the air, and does not choke up the cock) is thus easy enough. But things are different when *hard* pitch is to be run off. Here not merely must the pitch be allowed to cool down to some extent within the still, but it must first be run into a place protected from the air, in which it must remain till it gives off no more vapour and is no longer liable to take fire in contact with the air. Then it is let off into the open pitch-holes to solidify. In this case the outlet-cock of the tar-still should be provided with a cleaning-flange, and with some contrivance for heating it in order to melt the adhering pitch. This is best done at the end of each operation, before the still is charged again; it is then attended with much less danger than is incurred by deferring the heating till it is time to run off. For this purpose the plan shown in our diagram (fig. 76, p. 252) can be recommended. The cock is

placed in a recess of the still-wall; and at each side of it, separated from it by thin walls, the flues descend. If this should not keep the cock warm enough, a small fire of wood shavings can be made round the cock in the recess; or this is filled with sand which is heated by a small fire. Sometimes a steam-coil is wound round the cock; but steam-heat is frequently not sufficient for melting hard pitch. In any case the cock must be situated at the opposite side to the fire-door, lest the vapours given off from the running pitch be set on fire.

The outlet-cock is connected by a short descending pipe with an iron or brick spout covered over with an iron plate, for conveying the pitch into a chamber where it is to undergo its first cooling (the pitch-cooler). A spout is preferable to a pipe, unless the pitch-cooler is immediately beside the still, because the pitch readily solidifies in this part of its course, which does less harm when it takes place in a spout than in a pipe. The cover of the spout is covered over with earth to keep off the air and prevent cooling; but, for all that, there is always a coat of solidified pitch in it, which must be hacked out afterwards. If the air is not kept off here, the pitch may easily take fire; and the flame would travel to the pitch-cooler, in which case an explosion would be almost certain to follow. The spout must have sufficient fall and no sharp curves.

In the *pitch-cooler, pitch-oven,* or *pitch-house* the pitch must be left long enough (say five or six, or even twelve hours) to cease giving off vapours and to run no risk of taking fire when brought into the open air. This cannot be done without the pitch getting rather tough; hence a good deal of it remains behind in the pitch-cooler, and must be hacked out from time to time. The pitch-cooler is either a brick chamber with brick floor and arched top, or else any sort of iron vessel, for instance an old steam-boiler. A brick pitch-house for two 20-ton stills is about 20 feet long, 7 feet wide, and 8 feet high to the crown of the arch; some are very much larger than that. Each gable end is provided with a 3-feet-square man-hole, closed by iron doors luted with clay. At one gable end the pitch-spout enters; and at the opposite one there is a tap-hole just above the bottom, plugged with clay or with an iron bar, from which open spouts lead to the different pitch-holes.

Iron pitch-chambers are either cylindrical or square; they are more expensive, and suffer more by the hacking out, but cool

much quicker than brick chambers. The latter is no sensible advantage, since even in a brick chamber the pitch is cooled long before the chamber is needed for the next charge. Iron coolers, indeed, often act too quickly, and cause the pitch to solidify too early, so that they have been sometimes provided with a fireplace, which, however, may cause coking of the pitch. Where the pitch is softened in the pitch-cooler by adding creosote oil, there is of course hardly any trouble with solidifying.

The longer the pitch is left in the cooler, the less nuisance is produced; its temperature, on running out, ought not to exceed about 120°, and very little vapour is then given off. There is also this additional advantage, that the oily vapours, which cause the nuisance, are thus re-absorbed in the pitch, and make it softer, which means more valuable. But the longer the pitch remains in the cooler, the stiffer it becomes; if kept too long, the discharge-pipe becomes choked, in which case the workman generally clears it with a red-hot iron. This proceeding occasionally gives rise to an explosion, and can be entirely avoided by enclosing the discharge-pipe in a steam-jacket.

The pitch-cooler must have a vent in the roof for the escape of gas. This is mostly open to the atmosphere; but it is best to carry it to the chimney-shaft in a slanting tube, so that any condensing liquid may run back; or to make it dip about an inch into a vessel filled with water, similarly to the plan adopted in Paris (see below).

A tap adapted to viscid substances, such as partially cooled pitch, is shown in fig. 75.

Fig. 75.

F. Lennard (B. P. 4547, 1883) places within the (iron) pitch-cooler a number of wrought-iron pipes, through which cold tar is pumped so as to cool down the pitch, and to obtain a preliminary heating; or else he effects the same object by different arrangements of the pitch-cooler.

Sometimes no pitch-coolers are provided; the pitch is then left to cool in the still itself till it can be run straight into the open pitch-holes. This plan is decidedly not advisable for *hard* pitch; the stills must be allowed to rest much longer, and they must be cleaned out by manual labour after each operation.

Lastly, the *pitch-holes* or *pitch-bays* are situate in front of the pitch-house, and connected with it by brick or stone channels,

having a good incline and provided with movable covers. They must have a perfectly level brick floor and 18-inch side-walls; but otherwise their shape is quite indifferent and may be adapted to local circumstances. They ought to be of sufficient area to make it unnecessary for the pitch ever to fill them to a greater depth than 12 inches. There must be at least two of them, to serve in turn, so that at all times the pitch may completely cool down and solidify in one of them. In the heat of summer this is sometimes promoted by squirting water over. It is expedient to whitewash the floor every time before using it again, to make it perfectly smooth and to facilitate detaching the pitch. Hard pitch becomes so brittle that it is easily hacked up with a pick in large lumps. The dust unavoidably formed is most irritating to the mucous membranes of the eyes; the men ought therefore to protect their eyes by "goggles" or by crape; and this kind of work is always done by preference at night. In summer it is of course more disagreeable than in winter.

Watson Smith points out that the pitch-holes ought to be laid out so that no pools of rain-water can remain in them; otherwise the pitch may become honeycombed and much less saleable.

At some works the bays are entirely covered over with boards, or are enclosed in a galvanized iron chamber, provided with movable shutters, to avoid any nuisance.

At the smallest tar-works there are sometimes no pitch-bays, but the pitch is ladled or pumped out of the cooler into tubs, casks, &c. In this case explosions occur sometimes in running in pitch from the stills, just after a pitch-house has been cleaned from the solidified pitch by hacking it up (Hirsch, 'Chemiker-Zeitung,' 1884, p. 136), evidently because after that operation the pitch-house is filled with fresh air, which sets the pitch-vapours on fire as the contents of the still are running off.

Others ascribe the explosions occurring in pitch-coolers to the fine particles of carbon and pitch floating about in the air; but no doubt these alone would hardly be dangerous without the vapours equally filling the space. Blowing-out the cooler by dry steam after each operation would no doubt remove all danger from explosions.

Instead of the apparatus just described, a more complete arrangement has been made at the Paris gas-works—an arrangement proposed by Regnault, and which is also found at a large

English tar-works. It is represented in fig. 76. The pitch leaves the still by the cock *a* and a pipe *b* (provided with a cleaning-neck) and runs into the iron box *c*, in which it remains a few hours, till it has cooled down to 200°. From this it goes through the cock *d* and the pipe *e* into a wrought-iron chamber, *f*, half sunk in the ground, 7 feet wide, 30 feet long, and 10 feet deep, which receives the pitch of a number of stills. Along its whole length runs a brick pit, *h*, 5 feet deep, communicating with *f* by holes *g* near the bottom. An iron plate, *i*, prevents the pitch as it comes from *f*, at a temperature of about 120°, from rising at once to the surface; it can only pass along the edge of *i*. The pitch in *f* and *h* remains liquid from one operation to the next, being protected from quick cooling by the ground. But on the surface of the pitch above *i* a hard, elastic crust forms; this is promoted, if necessary, by running water over it. Now, if fresh, hot pitch runs out of *a*, it flows in *f* onto the surface of the partly cooled, but still liquid pitch from the last operation, forces this through *g* into *h*, the still colder contents of which rise past *i* and flow away underneath the crust at *k* into the open pits *l*, where they are left 8 or 10 days for entire solidification. The very hot pitch in *f* has in the interval time to cool down; the vapours rising from it and in *c*, which communicate by the pipe *m*, are condensed by the surface of iron in contact with the air, and are reabsorbed by the liquid pitch. The pipe *n*, which dips into a vessel filled with tar, allows the air to escape as the tar runs in, and also serves as a kind of safety-valve. But, besides, *f* is provided with a loose manhole-lid, merely luted by Scott's cement &c., which likewise performs the office of a safety-valve. This apparatus completely does away with all danger of fire, and with the nuisance arising from the heavy yellow or white, extremely irritating vapour given off by the hot pitch, which will travel as a compact cloud near the surface of the ground to great distances. Whilst observing that pitch was being run off, by the flowing away of tough pitch from the hole *k*, I could not perceive the slightest smell, although standing close by.

These vapours are intensely disagreeable to most persons; but the Government Inspector, Dr. Ballard, reports that the only ill effect upon health that he heard of was that they sometimes produce headache, giddiness, faintness, nausea, and perhaps some oppression of the breathing, but never any very serious or permanent ill effects.

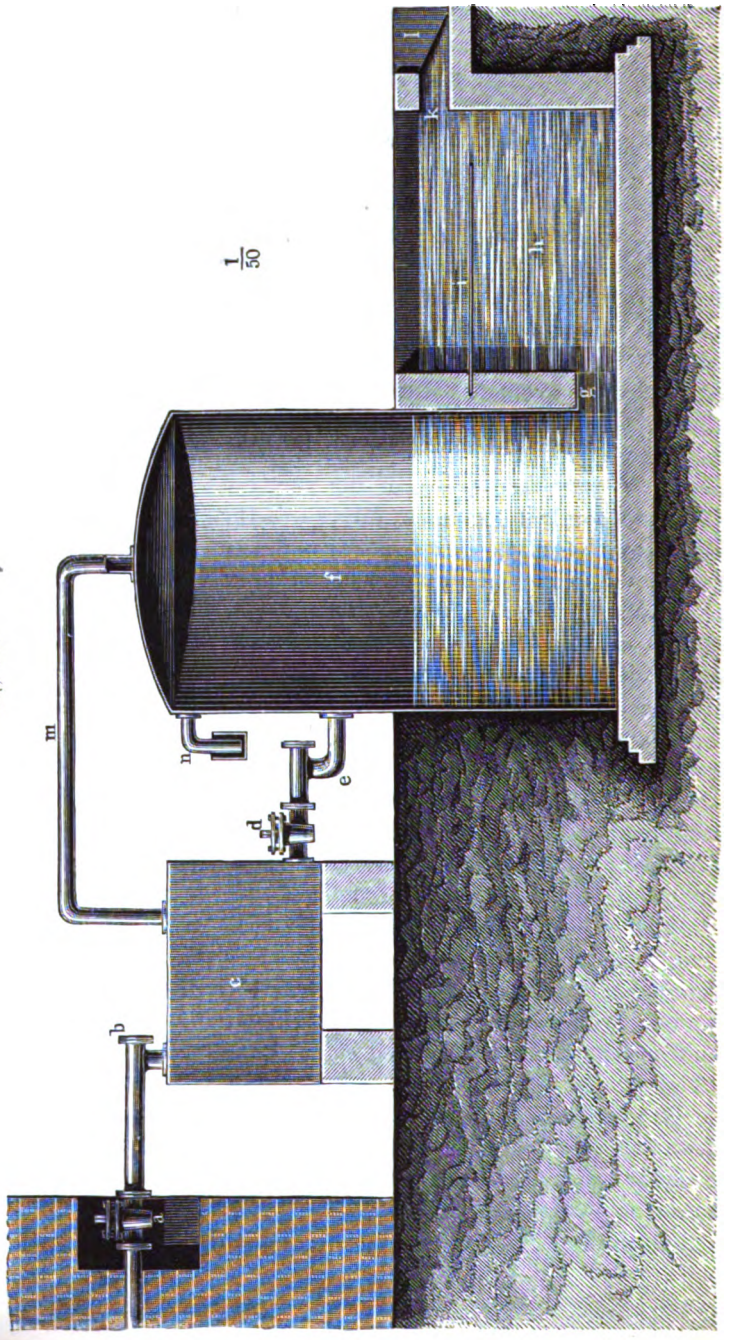


Fig. 76.

Continuous Distillation of Tar.

Several attempts have been made to render the distillation of tar a continuous operation, involving a constant inflow of fresh tar and outflow of pitch. Mallet* makes the tar circulate on a sufficiently long lead bath, where it successively gives off light and heavy oils, and at the end runs off as pitch. The fractionating is effected by making the tar pass round divisions which do not impede its circulation, but separate the vapours into two or three classes. According to Knab, there is nothing gained by this plan.

A proposal made by Vohl† is likewise intended to carry out a fractional distillation at a constant level, especially in order to meet the drawback of the light oils being kept back by the heavy ones. This is effected by the apparatus delineated in fig. 77. A and B are cast-iron stills; C, a feed-pipe dipping 3 or 4 inches into the liquid; D D, manhole-lids; E, pipe for conveying the vapours given off in A to B; F, pipe for the vapours going from B to the separator G; H, pipe for the heavy oils, connected with a refrigerator; I, pipe for the light oils, also connected with a worm; K, connecting-pipe between the two boilers, with the stopcock U, to be opened and shut by the handle L, in order to let the liquid flow from B into A. *m* and *n* are floats; *m* is so arranged that, on the liquid in A rising above the level *a*, the float shuts the supply-cock of C; *n* is connected with a loose valve which opens whenever the level rises too high. O, outlet-cock for the heavy-oil residue in A; P, fireplace; V, stoking-hole. To start the apparatus, A is filled through C up to the level *a*, its contents heated to boiling, and then a continuous supply run in through C. Until the ebullition in A is very strong, the flame is kept off B by a damper, and is directed straight to the chimney.

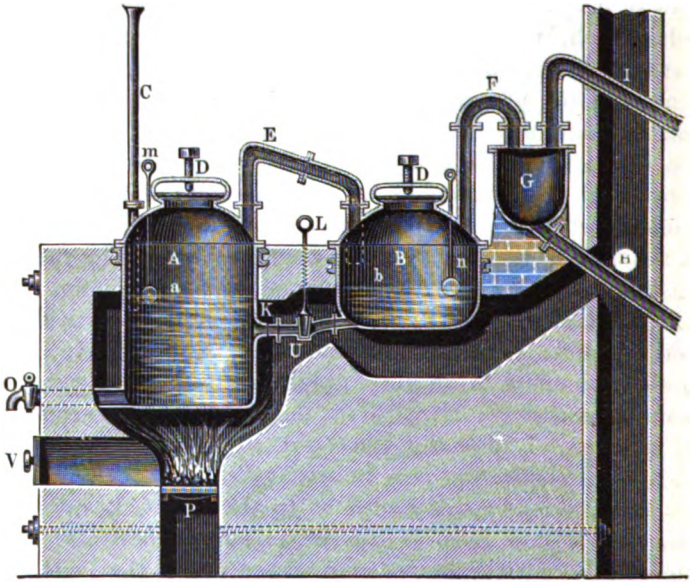
Meanwhile B and G are getting heated, and from H a constant stream of oil distils off. Now by opening the damper the fire from P is directed underneath B; and from this time light oils distil from I, heavy oils from H; the heaviest oils remain behind in B. If *m* shuts off the supply-cock, the fire must be increased. Also if the valve *n* in B is lifted, this is a sign of too little firing, too much being condensed in B; or else the damper keeping off the

* Girard & Delaire, 'Dérivés,' p. 11.

† Dingl. Journ. clxxvii. p. 133.

fire from B has been raised too late. When A has been worked off, which is soon known by experience, the fire is damped by wet

Fig. 77.



ashes and the residue from A let off through a refrigerator (consisting of a set of cast-iron pipes immersed in water) into a tightly covered iron vessel. Then the contents of B are run through U and K into A, the level is made up to *a* by supplying tar through C, the damper for B is let down, and the operation is recommenced. Such an apparatus (erected by Thiriart and Co. of Cologne) is said to yield 1½ ton of light oils in 12 hours. It was originally intended for paraffin oils; but Vohl believes that it is also eminently suitable for coal-tar, and would yield twice the usual quantity of benzene and its homologues.

N. M. Henderson (B. P. 540, 1883) has constructed a similar apparatus, consisting of three horizontal cylinders, about 7 feet diameter and 9 feet long.

Distillation of Tar for the purpose of making Illuminating-gas.

The present enormous depression of prices, even for the most valuable constituents of coal-tar, has led to a proposal to distil it expressly in such a way that only those substances are removed which are injurious to the object in question, while all the others, including benzol, are converted into a rich gas. Davis* states that gas-tar oils, as well as petroleum spirits and petroleum residues, become gasified when being passed over red-hot surfaces, and that about 50 cubic feet of 50-candle gas are obtained thereby from one gallon, possessing a spec. grav. of 0·912. Taking the oils as weighing 10·8 lbs. per gallon, one ton would yield 16,600 cubic feet of 50-candle gas, approaching very nearly the composition of rich cannel-gas. In order to carry out this process of enrichment on a practical scale (say for works carbonizing 50 tons of coal per day) a set of three 10-ton tar-stills would have to be provided, so that they might be worked in sequence, one always being run off and refilled. The raw tar is distilled in the usual manner and the distillate conveyed into three separate tanks, A, B, and C, the still being stopped when a sample of the pitch, on being withdrawn, twists easily at a temperature of 55° C., which signifies that it is of very good quality and easily saleable (comp. Chap. VI.). The contents of tank A will remain liquid; those of tank B will, on cooling, separate naphthalene, and those of tank C crude anthracene. If tank B is constructed in the form of a filter, the naphthalene can be easily removed, and either worked up, sold, or used as fuel. The oils of tank C must be filter-pressed to recover the anthracene, after which the contents of all are ready to be made into gas. When sufficient oils have accumulated, another of the stills is filled with a mixture from the tanks A and B, and this is slowly distilled, the vapours being passed directly into one end of a through retort heated to dull redness; the gasified hydrocarbons passing out at the other end by means of the ascension-pipe are mixed with the gas from the ordinary retorts. When four fifths of the contents of the still have been vaporized, the fire is withdrawn and the still filled up with raw tar, which is distilled as before, and the pitch run out for sale; after which the still is again ready for vaporizing another batch of oils. When sufficient

* Journ. Soc. Chem. Ind. 1886, p. 6.

oil from the anthracene has accumulated, it is distilled in whichever still happens to be at liberty. The first fourth is run into the creosote or B tank, the second fourth into the anthracene or C tank, the still being stopped when the pitch will just soften at 50°, when it is run off into the pitch-house in the same manner as when dealing with ordinary tar. In this way every gas-works would be able to supply an illuminating-gas of good quality without the aid of cannel-coal, and to be a producer of pitch and anthracene of the very best quality.

The calculation would run as follows :—

100 tons of ordinary coal give each 10,000 cubic feet of gas of 17 candles.

5 tons of cannel-coal give each 12,000 cubic feet of gas of 28 candles.

Coal produce 1000×17 candles..... 17,000.
Cannel „ 60×28 „ ..... 1,680.

In all 1060 at 17·6 candles.

Taking coal and gas-tar :—

100 tons of coal give 10,000 feet of 17-candle gas.
2·8 „ tar-oils give 16,000 feet of 50-candle gas.
Coal produce 1000×17 candles=17,000.
Tar-oils „ $46{\cdot}5 \times 50$ candles= 2,325.

In all 1046·5 at 18·4 candles.

Davis thus makes out that the 7 tons of tar produced from 100 tons of coal [this is much in excess of the average!] has a value to the gas-maker equal to nearly 10 tons of cannel-coal. One through-retort will give about 500 cubic feet of gas per hour, equal to the decomposition of some 7 gallons of oil per hour.

Davis's statements are most emphatically contradicted by an impartial and very competent observer, Lewis T. Wright*. He shows that very little is to be gained by incorporating all the benzene of coal-tar with the gas. Taking the percentage by weight of benzol in coal-tar=0·8, the percentage of tar on the coal as 6·6, and the quantity of gas to be carburetted per ton of coals as 10,000 cubic feet, we have as the total quantity of coal-tar benzol available per 10,000 cubic feet 0·1183 lb. Since it takes 1·9 lb. of benzol to bring 16-candle gas up to 17 candles, the above quantity of benzol only amounts to an enrichment of 0·06 candle,

* Journ. Soc. Chem. Ind. 1886, p. 561.

which is evidently unremunerative. Neither does the dry distillation of tar-oils lead to the solution of the problem. Wright made many experiments, injecting the oils into a retort packed with lumps of caustic lime, kept at an orange-red heat, and passing the gas there generated through a second similar retort. He thus obtained from *crude naphtha* as highest illuminating-power 10,130 cubic feet of gas of 20½ candles. The greatest yield of gas was 27,100 cubic feet of 14½ candles; when the yield of gas fell as low as 6000 to 8000 cubic feet per ton the illuminating-power did not rise above 20 candles. The gas from *light oil* in sixteen experiments ranged from 18,000 to 30,000 cubic feet per ton; the illuminating-power from 16 to 13½ candles. The highest illuminating-power obtained with *creosote oil* was 14 candles with a make of 13,300 cubic feet; the greatest yield of gas 29,300 cubic feet per ton, with an illuminating-power of 8½ candles. In all these experiments with tar-oils continual stoppages took place from obstinate accumulation of naphthalene in the pipes, which seems impossible to avoid in practice; but apart from that, the comparatively low yield and the very low illuminating-power of the gas seem to preclude the use of tar-oils for gas-making even at the present low prices. Crude tar, treated as above in retorts charged with lumps of lime, yielded on an average 10,700 cubic feet of 12½-candle gas; and Wright regards tar as a gas-making material dear as a gift.

Results of Work.

In the case of tars of well-known quality the *duration of the distillation* and *the quantity of the distillates* furnish valuable indications for changing the receivers. The former must evidently vary much, according to the size and even the shape of the stills. I have received the following statements respecting it.

In Paris the distillation of 6½ tons lasts 31 or 32 hours, cooling included. The first runnings and light oil run 14 hours. The necessary fuel amounts to 50 cubic feet of "agglomerated coke" (patent fuel made from coke breeze).

At a London works a still of 2000 gallons (say 10 tons) capacity is worked off every 24 hours. 14 hours are reckoned for the distillation, 10 hours for cooling down, running the pitch, cooling again, and recharging.

Very small stills, of 1200 gallons (=6 tons) capacity, are all finished in 11 or 12 hours. The fire is slackened an hour after commencing; an hour later the distillation begins, and the heavy oils six hours after that.

At one German works the horizontal 18-ton stills take 52 hours for working off, and 12 hours for cooling. At another the stills (very large, holding 40 to 50 tons) take only from 36 to 42 hours for working off and 6 hours for cooling. At a third works 25-ton stills take 36 hours.

At an English works known to me the first runnings from a 22-ton still take 10 hours, the light oil (up to sp. gr. 1·0) 6 hours, creosote oil (including anthracene oil) 12 or 14 hours, cooling down till the pitch is run off 12 hours. Immediately after, the stills are recharged.

According to Watson Smith, in Lancashire 20-ton stills (steam being employed at the close) were worked off 4 times per week when anthracene oil was not worked for,—in the other case, 3 times per week, or 7 times per fortnight. 10-ton stills are worked off 6 times per week.

In the following tables the *yields* of the different fractions from coal-tar, from various sources, are given. But these data are not directly comparable with one another, as we have seen that the fractionating is not done in the same way in all.

To simplify matters, I shall at the same time quote the quantity of the final products, wherever they are stated.

Average of my own Results with 1 *ton of Tar from the Midland Counties.*

Ammoniacal liquor ...	3 gallons.
First runnings	5·5 to 8, average 6·33 gallons.
Light oil	13·5 to 15 gallons.
Creosote oil	68 gallons.
Pitch (hard).....	11 cwt.

Final Products from the same.

	Average.	Minimum.	
50-per-cent. benzol	3·30	3·06	gallons.
Best naphtha	2·40	2·48	,,
Burning naphtha.....	1·50	1·62	,,
Creosote oil directly distilled	68	.....	,,
,, ,, total	80	80	,,
Pitch (hard)	11 cwt.	11 cwt.	

According to Stohmann-Kerl's 'Chemie,' 3rd ed. vi. p. 1169 :—

	South-German tar.	North-German tar.	
	per cent.	per cent.	
		a.	*b.*
Light oil	10·5	8·4	8·9
Middle oil	...	9·4	10·6
Creosote oil	27	23·9	24·6
Pitch	57	50·9	50·9
Ammoniacal liquor and loss	5·5	7·4	5·9

According to Thenius (Deutsche Industrie-Zeit. 1865, p. 292) :—

	Ordinary gas-tar.	Tar made as principal product.	Tar obtained on purpose by distilling coal with superheated steam.
	per cent.	per cent.	per cent.
Ammoniacal liquor	4·0	4·00	6·22
Light oil (sp. gr. 0·900)	4·0	30·32	25·34
Creosote oil (sp. gr. 1·020)	32·0	38·13	32·53
Paraffin oil	.....	.....	13·68
Pitch	56·0	18·75	16·03
Gases and loss	4·0	8·50	6·20

According to Wurtz ('Matières colorantes') 1000 kilog. tar, value 90 francs, yield :—

	a.	*b.*	*c.*	
	kg.	kg.	kg.	fr.
Ammoniacal liquor	...	14	14	
First runnings	18–20	20–40	20 =	10·00
Light oil		70–80	70 =	35·00
Creosote oil	240–260	320–350	320 =	48·00
Anthracene oil, 10-per-cent.	9·5–10	100–110	100 =	60·00
Pitch	660–650	350	350 =	17·50
				170·50

[The enormous difference between the columns *a* and *b* is inexplicable. It seems hardly credible that tar could be worked down

to 35 per cent. of even very hard pitch. Neither can 100 kilog. of 10-per-cent. anthracene oil, *i. e.* 1 per cent. of real anthracene, be obtained.]

Tar from the Berlin Gas-works (Chemische Industrie, 1879, p. 282).

	per cent.	per cent.
Benzol (including toluene &c.)	0·80	
Other colourless oils (higher homologues)	0·60	
Crystallized carbolic acid	0·20	
Cresol for disinfecting purposes	0·30	
Naphthalene	3·70	
		5·60
Creosote oil		24·00
Anthracene (pure)		0·20
Pitch		55·00
Water and loss		15·20
		100·00

The following statements are from 'Chemistry, by Writers of Eminence,' Mackenzie, i. pp. 500 and 506.

The average produce from 1200 gallons of tar (about 6 tons) is :—

		per cent by weight.
Ammoniacal liquor	about 50 gal. = about	4
First light oils	„ 20 „ „	1·5
Second light oils	„ 20 „ „	1·5
Creosote oils	„ 250 „ „	22
Anthracene oils	„ 50 „ „	4
Pitch	„ 4 tons „	67

According to Letheby, 1 ton of gas-coal, as distilled in London, gives about 9 to 10 gallons of tar; 1 ton of coal as distilled in the provinces gives about 15 gallons of tar; 1000 gallons of London tar yield :—

Ammoniacal liquor	20–28 gal.,	average 24 gal.
Crude naphtha (first light oils)	12–20 „	16 „
Second light oils	4·8–14 „	12 „
Creosote oils	275–296 „	288 „
Pitch	3·2–4 tons, „	3·5 tons.

After purification these light oils yield :—

	gallons.	
40-per-cent. benzol...	3·44	} =6·84 at 90 per cent.
90 „ „ ...	5·31	
Solvent naphtha.....	4·18	
Last runnings	1·2	
Total dead oils	301·87	

A. J. Dickinson gives as the average yield from 1000 gallons of London tar :—

	gallons.	per cent. by volume.
Naphtha (containing 6 per cent. benzol)	30	3
Ammoniacal water.....	30	3
Anthracene (at 25 per cent.).....	10	1
Pitch	650	65
Creosote, lubricating-oils, carbolic acid .	280	28

The figures given by Letheby and Dickinson are somewhat different from the following figures, given on oath, in the course of a law-suit, as the average yield of London tar (supplied to me by the kindness of Mr. S. B. Boulton). The first column represents the results obtained at the Silvertown works of Messrs. Burt, Boulton, and Haywood ; the second, those obtained at the Beckton works of the Gas-Light and Coke Company (these two being among the largest tar-distillers of the world). In the first column all the oils are dehydrated and the water is included in the percentage of ammoniacal liquor :—

	Silvertown.	Beckton.
Ammoniacal liquor.....	4·16	2·00
Crude naphtha	1·50 of 45% at 120°	1·66 of 30% at 120°
Light oil	1·16	1·62
Creosote (containing naphthalene)...	14·16	15·70
Anthracene oil (strained or green oil)	14·00	18·83
Anthracene, 300 per cent.	1·80	1·90
Pitch.....	60·00	56·29
Loss	3·22	2·00
	100·00	100·00

Watson Smith obtained in 1869, from Lancashire tar [mostly made from cannel coal], as follows. 1000 gallons of tar of sp. gr. 1·16=5·3 tons, yield :—

		per cent. by weight.
Ammoniacal liquor (4-per-cent.)	25 gal., =	2·2
First light oils	28 „ =	2·2
Second light oils	131 „ =	10·6
Creosote oils	87 „ =	7·6
Anthracene oils	191 „ =	16·9
Pitch	3¼ tons, =	60·5

On further rectification these distillates yield:—

90-per-cent. benzol	about 6 gallons.
Solvent naphtha	„ 74 „
Carbolic acid	„ 6½ „
30-per-cent. anthracene	0·50 cwt.
Equal to pure anthracene	0·15 „

The following table of the products of a 20-ton still, by Watson Smith*, is very instructive. The tar (from Lancashire) was of sp. gr. 1·167 at 15½° C. The still held 3672 gallons = 19⅛ tons. The fractions were collected singly, one after another (except only Nos. 1 and 2, collected at the same time):—

	gal.		sp. gr.	
1.	100	first runnings	0·897	at 10° C.
2.	90	ammoniacal liquor (4-per-cent.)		
3.	100	light oil (including carbolic oil)	0·932	„ 16
4.	100	light oil	0·960	„ 22
5.	100	„	0·980	„ 22
6.	100	„	0·991	„ 29
7.	100	„	1·010	„ 24
8.	100	„	1·014	„ 28
9.	100	creosote oil	1·021	„ 28
10.	100	„	1·025	„ 23
11.	100	„	1·031	„ 24
12.	100	„	1·034	„ 25
13.	100	„	1·043	„ 25
14.	100	„	1·048	„ 22
15.	100	red oil	1·059	„ 24
16.	100	„	1·066	„ 30
17.	100	„	1·085	„ 33

The fractions 9 to 11 on cooling yielded considerable quantities of naphthalene; the rest, beginning from 12, were put aside to

* Private communication.

crystallize for anthracene. But from fractions 12 to 14 little or nothing crystallized; only the "red oils," from 15 onwards, deposited crude anthracene on standing. By three distillations, 2·617 per cent. of the oil, or 0·35 per cent. of the tar, of crude anthracene cake were obtained from these oils.

The pitch weighed 11·48 tons; from this, again, 0·556 per cent. (=0·33 per cent. on the tar) of anthracene cake could be obtained.

From a charge of 6·2 tons of Wigan cannel-coal-tar Watson Smith obtained:—

First runnings	29 gallons,	sp. gr.	0·919
Light oils	100 „	„	1·000
Ditto	100 „	„	1·019
Creosote oil	220 „		
Red oil	295 „		
Pitch	4 tons.		

The creosote oil was clear; and on cooling only traces of naphthalene separated; a little paraffin was also present.

He obtained the following results from Manchester tar:—

	Price in 1870.
Employed, 19·125 tons of tar.....	@ 25*s.* per ton.
Obtained:—11·475 „ pitch.....	@ 20*s.* „
0·137 „ crude anthracene.....	@ 1*s.* per lb.
1360 gal. creosote oil	@ 1*d.* per gal.
30 „ crude carbolic acid (extra good).....	@ 3*s.* „
149 gal. rectified solvent naphtha...	@ 1*s.* 6*d.* „
55½ „ 50-per-cent. benzol	@ 2*s.* 6*d.* „
90 „ ammoniacal liquor	(3 per cent.).

The materials required for distillation and purification were:—

10 tons of coal for the still, steam, &c.
14½ gallons concentrated sulphuric acid.
10¼ „ brown acid (at 140° Tw.).
2 cwt. 1 qr. caustic soda (60 per cent.).
2 to 3 cwt. quicklime.

According to Watson Smith, the richest and best tar comes from small gas-works, because there the greatest possible yield from the coal is not, as at the large works, a primary consideration. There are contractors who drive about in the country buying up such small lots of tar and gas-liquor, and taking it to the tar-distillers for sale.

The following table, compiled by Sir Henry Roscoe from statements collected by Messrs. Watson Smith and I. Levinstein, represents the average yield of products from Lancashire tar, together with some interesting statements concerning the dyeing-power of the artificial colours derived therefrom *.

One ton of Lancashire Coal yields, when distilled in Gas-retorts, on an average :—

Gas (cubic feet).	Ammoniacal liquor, 5° Tw.	Equivalent to Ammonium sulphate.	Coal (gas)-tar, sp. gr. 1·16.	Coke.
10,000	20 to 25 gallons.	30 lb.	12 gals. = 139·2 lb.	13 cwt.

Twelve gallons of Gas-tar yield (average of Manchester and Salford Tar) :—

Benzene.	Toluene.	Phenol proper.	Solvent Naphtha for Indiarubber, containing the three Xylenes.	Heavy Naphtha.
lb.	lb.	lb.	lb.	lb.
1·10	0·90	1·5	2·44	2·40
= Aniline	= Toluidine		yielding	
1·10	0·77		0·12 Xylene =	
			0·07 Xylidine.	
= Magenta 0·623.		Aurin		
or 1·10 lb. Aniline yield 1·23 lb. Methyl Violet.		1·2		

Naphthalene.	Creosote.	Heavy Oil.	Anthracene.	Pitch.
lb.	lb.	lb.	lb.	lb.
6·30	17·0	14	0·46	69·6
= α Naphthylamine				
5·25				
= α or β Naphthol				
4·75				
= Vermilline Scarlet, RRR				
7·11, or			Alizarin.	
= Naphthol Yellow †			20%	
9·50			2·25	

* Lecture delivered at the Royal Institution, April 16, 1886, p. 7.

† The naphthol-yellow is a representative colour from α naphthol, while the vermilline scarlet is a representative colour from the combination of α naphthylamine with β naphthol.

Dyeing-powers of Colours from 1 *ton of Lancashire Coal.*

lb. 0·623 Magenta dye 500 yards 27 inches wide Flannel a full shade.	lb. or 1·23 Methyl Violet dye 1000 yards 27 inches wide Flannel a full Violet.
lb. 9·50 Naphthol Yellow dye 3800 yards 27 inches wide Flannel a full Yellow.	lb. or 7·11 Vermilline. dye 2560 yards 27 inches wide Flannel a full Scarlet.
lb. 1·2 Aurin dye 120 yards 27 inches wide Flannel a full Orange.	lb. 2·25 Alizarin 20% dye 255 yards Printer's cloth a full Turkey Red.

Dyeing-power of Colours from 1 *lb. of Lancashire Coal.*

Magenta or Violet		Yellow or Scarlet	
a piece of Flannel 8 in. by 27 in.	a piece of Flannel 24 in. by 27 in.	a piece of Flannel 61 in. by 27 in.	a piece of Flannel 41 in. by 27 in.
Orange a piece of Flannel 1·93 in. by 27 in.		Turkey Red a piece of Flannel 4 in. by 27 in.	

The following statistics have been kindly supplied to me by Mr. Wilton, manager of the Beckton tar-works, as representing the production of the United Kingdom in 1885 :—

	gallons	= tons.	
Ammoniacal liquor from tar alone...	3,600,000	1200	(of sulphate)
Carbolic acid (crude)	600,000		
Creosote oil	21,600,000		
Of this there was liquid creosote	10,800,000		
„ „ creosote salts		56,620	
(=crude naphthalene) corresponding to pure naphthalene.....		25,310	

	gallons	=	tons.
Green oil	20,400,000		
Benzol and toluol	1,500,000		
Solvent naphtha	620,000		
Anthracene (pure) = 6,840,000 units =			3,420
Pitch			396,000

Total quantity of tar distilled 120 million gallons; say 645,000 tons.

A statement in the 'Chemiker Zeitung' (1879, p. 148) puts the yield from 11250 litres (=10 tons) of London tar at:—

50-per-cent. benzol	12·96 litres	=	1·1 per cent.
Solvent naphtha	12·15 „	=	1·0 „
Burning naphtha	16·75 „	=	1·4 „
Creosote oils	373·5 „	=	35·0 „
Anthracene cake (30 per cent.)	11·25 „	=	1·0 „
Pitch	5870 kilog.	=	58·6 „

Crace Calvert* gives as the yield from the tar of

	Light oil.	Neutral heavy oil.	Phenol.	Paraffin.	Naphthalene.	Pitch.
	per cent.	per cent.	per cent.	per cent.	per cent.	per cent.
Boghead	12	30	3	41	...	14
Cannel coal	9	40	14	...	15	22
Newcastle coal	2	12	5	...	58	23
Staffordshire coal	5	35	9	...	22	29

(All the treatises repeat these statements without pointing out how absurd they are on the face of them. To mention only two things, how is it that all the products sum up to 100 per cent., as if tar could be distilled without any loss? and is it really credible that Newcastle tar contains only 19 per cent. liquid products, along with 58 per cent. of naphthalene and 23 of pitch?)

According to Häussermann (Industrie der Theerfarbstoffe, 1881, p. 13), 100 parts of tar from German coals yield

5–8 per. cent. light oil,
25–30 „ creosote oil,
8–10 „ anthracene oil,
50–55 „ pitch.

* Compt. Rend. xlix. p. 262.

The final products are

0·6	per cent.	benzene,
0·4	„	toluene,
0·5	„	higher homologues,
8–12	„	pure naphthalene,
5–6	„	phenol,
0·25–0·3	„	anthracene (pure).

According to G. Schultz ('Chemie des Steinkohlentheers,' 2nd ed. vol. i. p. 67) there were obtained, in a Rhenish tar-works, from 100 parts of tar:—

Purified benzol (for aniline and as a detergent)	1·00
Pure anthracene	0·33
Pure naphthalene	2·00
Creosote oil	30·00
Pitch	60·00
Ammoniacal liquor	2 to 10·00

Analyses of the *tar from Coke-ovens*, &c., have been quoted, pp. 59, 81, 82, 84, 89.

Testing of Tar.

If a sample of tar has to be tested for its yield on a smaller scale, its distillation must be carried on in exactly the same way as on the large scale. The result will be all the more reliable the larger the scale of the testing-operation. When distilling, say, 10 gallons, the results will be only approximative, especially for benzol and naphtha. It is better to employ small stills holding 80 to 100 gallons; but it is even preferable to distil 200 or 250 gallons from a light-oil still (Chapter X.). The products are respectively weighed and measured; and light oil and naphtha are tested for their yield of benzol and naphtha according to the rules given at the close of Chapter XI.

Where the testing of tar must be performed with ordinary laboratory appliances, the following hints, by Watson Smith*, will be found extremely valuable, and are therefore quoted *in extenso*:—

"It is well known to those who have attempted the distillation

* Journ. Soc. Chem. Ind. 1883, p. 496.

of samples of coal-tar (wood-tar is just as difficult to manage) that, owing to the invariable presence of water, often in considerable amount, there is extreme difficulty in the earlier stage of the process in preventing boiling or frothing over of the contents of the retort. Sometimes disproportionately large iron retorts are used for such trials of small quantities of tar, in order to leave as much room as possible for frothing up. By the method about to be described, we have used, in the laboratory of the Owens College, only large glass retorts, holding about $2\frac{1}{2}$ litres, when filled to within $\frac{3}{4}$ of an inch of the beak of the retort, and have found no difficulty in fractionating the tar in such apparatus, when the proper precautions were observed. The following are the salient points in the method I have devised :—

"The tar is first freed from water as much as possible, by placing the containing vessel (*e. g.* a large glass beaker) in hot water, and allowing to stand for about a day and night, the beaker being well covered with a glass plate. The reduction thus effected of the density and tenacity of the tar allows of the separation of water with greater facility. If the tar be heavier than water it settles down, and the water rises, forming a layer, which, after allowing to cool, may be decanted off. Frequently a great deal of water may be got rid of by inclining the vessel alternately in different directions, when, if the tar be a heavy one, the water collects and flows to the point of inclination more rapidly, and so the portion accumulated may be decanted off before the tar reaches that point. In the case of a tar or tar-oil lighter than water, a subnatant layer of water forms by the warming and settling process; and in this case a tolerably wide siphon or run-over might be used, or, from a beaker, the tar-oil might be merely decanted." For the *specific gravity determination*, "a measured quantity of tar (say 1 litre), settled or partially dehydrated as above, is run into a previously tared vessel, and, after cooling to 15° C., the latter, with its contents, is weighed. These data are sufficient for the specific gravity. The ordinary specific-gravity bottle would be a clumsy contrivance in this case. For the *distillation* about $2\frac{1}{2}$ litres of tar were taken and poured into a large glass retort arranged on a stand in the usual way. The stand is placed in a large iron tray with high sides (about 6 to 7 inches), the bottom of which is covered with sand to the depth of $\frac{1}{2}$ an inch or so. This arrangement is to afford protection to the operator, in case of accident. A glass

tube, besides the thermometer, is inserted through the cork acting as a stopper. This tube is drawn out to a small aperture, and is caused to dip about halfway to the bottom of the retort from the surface of the tar. A slow current of air is passed through the tube and forced through the tar, and the temperature of the tar is carefully and not too quickly raised to from 60° to 70° C. This temperature is maintained, if necessary, for a day or two, until all ammonia-water is expelled. If the tar be a heavy one, a layer of ammonia-water may form on its surface after heating to 60° to 70° for some time. If the layer be of considerable thickness, it will be advisable to remove the stopper and decant it off. Frequently a slow distillation for about a day or more may thus be spared by an operation lasting a few minutes only. If the tar contain much spirit or benzol, the receiver, which should be one with a second opening admitting a cork, is connected with a wash-bottle containing some heavy oil, to retain naphtha vapours else carried off by the air-current. The naphtha is afterwards recovered by blowing wet steam through the oil, the vessel being connected with a condenser. The volume of the naphtha is then measured. When all water is removed from the tar, the distillation will proceed quite smoothly."

In my own practice I have found it convenient to place the retort in a thin iron capsule with high sides, containing no more than half an inch of sand at the bottom; the projecting part of the retort is enveloped in wire-gauze, and the disk is heated by a very powerful gas-stove, so that at the end of the operation it becomes red-hot. Otherwise the prescriptions given by Mr. Watson Smith were found to be very useful.

CHAPTER VI.

PITCH.

We have seen in the last Chapter that the distillation of coal-tar leaves a more or less consistent residue, according to the way in which it has been carried on. If only the light oil is distilled off (that is, if the process ceases when the specific gravity of the distillate equals that of water), the residue in the retort (about 80 per cent. of the weight of the tar) is sometimes called *asphalt* (*brai liquide*). It is very unusual now to carry on the process in this way; what is called "asphalt" by tar-distillers is made by mixing ordinary pitch with a suitable quantity of creosote oil, and most commonly it is soft pitch mixed with sand &c. (see below).

If about 10 per cent. more is distilled off, the residue is *soft pitch*; next comes moderately hard pitch; and *hard pitch* is obtained, if the process is carried on as far as wrought-iron vessels will permit (p. 237). Another rule is this: *Soft pitch* is obtained if the distillation is interrupted before driving off the anthracene, when the specific gravity of the distilling oils is about 1·090; *hard pitch*, if it is continued till the oils show sp. gr. 1·120; moderately hard pitch, if the distillation is interrupted between these two stages.

The "asphalt," if obtained by merely distilling off the light oils, naturally contains all the constituents of creosote oil (that is, naphthalene, phenols, &c.), along with all higher-boiling substances. Proper "pitch" always contains the least volatile components of coal-tar, such as anthracene, phenanthrene, chrysene, pyrene, &c. (comp. p. 128 *et seq.*), together with several ill-defined substances, as bitumen, &c., and free carbon, or rather coal-dust or coke-dust in an extremely fine state of division. It is, however, possible that something very nearly equal to real carbon, or graphite, formed by the decomposition of tar-oils on the hot sides of the

retorts, is also present in coal-tar. The value of coal-tar is greatly diminished if there is a considerable quantity of such "free carbon" present, in which name is always comprised coal-dust or coke-dust as well (comp. pp. 159 & 241).

Behrens*, by successively digesting hard pitch, freed from all oils up to spec. grav. 1·120, with cold benzene, carbon bisulphide, boiling benzene, and boiling alcohol, obtained 23·54 per cent. of a black powder, containing 90·836 C, 3·058 H, and 0·398 ash; when treated a little differently, the residue yielded 91·921 C, 3·157 H, and 0·872 ash, quite similar to South Welsh anthracite (compare the patent of E. Heusser, lower down).

According to Habets†, good hard pitch consists of 75·32 per cent. C, 8·19 H, 16·06 O, 0·43 ash, and its specific gravity is 1·275–1·286.

Hard pitch is easily divided into flakes or lumps, which do not soften even in the sun, and can be always sent out in bulk, whether in railway-trucks or in ships, at all seasons of the year. Moderately hard pitch can be sent out in bulk in railway-trucks, but not in ships, where it would coalesce into a mass, at least in the warm season. Hence the English tar-distillers mostly make hard pitch; and so do the French, at least in summer. Soft pitch can only be sent out in casks, and is mostly run into these directly from the tar-stills.

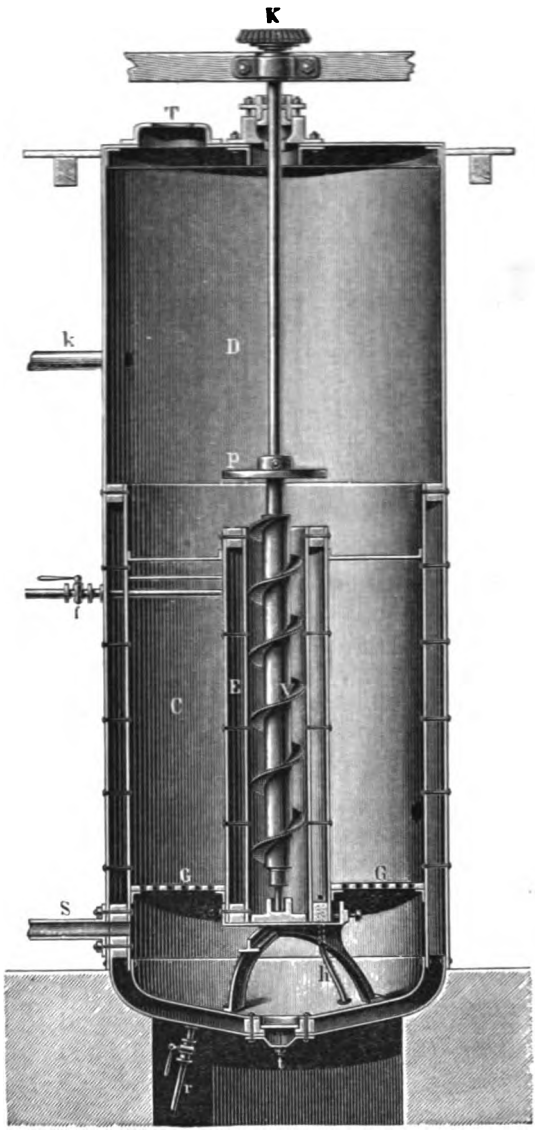
The manufacturers of patent fuel, especially in Belgium, greatly prefer soft pitch to hard; hence the German tar-distillers are compelled to make at most only moderately hard pitch.

When it is not feasible to soften the pitch while still liquid in the still, or else in the pitch-cooler, by pumping in oils, the operation is more complicated. This occurs when hard pitch has to be softened by the buyer to make it more suitable for the manufacture of patent fuel. For this purpose special *pitch-revivifying apparatus* have been constructed. Such an apparatus, as employed at the Blanzy coal-mines, is described in Payen's 'Précis de Chimie industrielle,' 1878, ii. p. 919, as follows:—In fig. 78, C is an upright boiler, 6 feet in diameter, 9 ft. 2 in. high, holding about 320 cubic feet, and provided with a steam-jacket. In the centre revolves an endless screw V, surrounded by an annular casing, which is heated by steam entering at *f* and issuing at *h*

* Dingler's Journal, vol. ccviii. p. 369.

† Gurlt, 'Steinkohlenbriquettes,' p. 23.

Fig. 78.



into the outer jacket; the condensation-water is discharged by *r*. At the bottom are the annular gratings G G (made of perforated iron plate) for retaining large pieces, the pipe S for discharging

the revivified pitch, and a cleaning-hole (*t*). The boiler C is surmounted by a wrought-iron chamber, D, of equal size, to receive the froth formed during the operation. Here is a manhole, T and a gland for the passage of the screw V. The work is carried on in this way. A certain quantity of tar, creosote oil, or the like is let into the apparatus through the pipe *k*; steam is admitted till the heat rises to 150°; the screw is made to revolve; and the pitch which is to be revivified is gradually charged through the manhole T. More tar and pitch are added till the boiler contains about 9 tons of materials. The plate P prevents the pitch thrown in at T from falling upon the screw. The pitch is soon melted in the hot tar, the mixture passes through the sieve G, is lifted by the screw V, and thrown out again on the top. After eight hours all is melted and homogeneous; now the discharge-cock is opened and the revivified pitch run into coolers, after which the operation can be commenced anew.

The revivification can be effected by means of creosote oil, naphthalene, or tar which is merely deprived of the light oil (=asphalt). It has been found at Blanzy that the creosote oil does not modify the agglomerating property of pitch, but merely renders the pitch more liquid; naphthalene increases the agglomerating property, but causes solidification at too low a temperature; the best of all is tar deprived of light oils, of which 10 or 20 parts are taken for 100 of pitch. [Probably the last tar-oils, deprived of anthracene, would be still better.]

Coal-tar pitch is an excellent *reducing-agent* (*e. g.* for black-ash mixing, for making barium sulphide, &c.), because it is nearly free from ashes and sulphur; but it is mostly too expensive for this purpose.

As a factor in the manufacture of *cement-steel* (blister-steel) it has been patented by E. J. Payne and W. Clarke (Oct. 5, 1872). It is contended that the iron will combine more quickly with the carbon from pitch than with that from any other source.

The principal employment of coal-tar pitch is for making *patent fuel* (*briquettes*) from small coal or coke-breeze. A detailed description of this industry does not come within the scope of this treatise; a number of special treatises have been written upon it, as the French one by G. Franquoy (1860) and the German ones by Gurlt ('Die Bereitung der Steinkohlenbriquettes,' Braunschweig, 1880) and by Jünemann ("Die Briquetteindustrie," Hartleben's

Verlag); and the technical cyclopædias also contain much information upon this subject, of which we shall only give the outlines here.

This industry would appear to be due to Ferrand and Marsais, who, in 1832, obtained a French patent for employing coal-tar for this purpose. Marsais since 1842 employed soft pitch, and in the same year founded the works at Bérard, near St. Etienne. Hard pitch was used in 1843 in England by Wylam, and since 1854 in France. The patent fuel made near St. Etienne was sold by the name of "péras."

The manufacture of patent fuel is the most natural outlet for the immense quantities of small coal (slack, duff, &c.) obtained at the majority of coal-pits, and saleable only at a very low price or sometimes not at all. It is remarkable that this industry has principally developed itself in France and Belgium, but very much less in England and Germany, although there are enormous quantities of raw material available, for instance in Westphalia. The present production of patent fuel is estimated as follows (Schultz, 'Steinkohlentheer,' 2nd ed., p. 87) :—

	Number of Works.	Tons
France	31	1,000,000
Belgium	16	500,000
England	7	300,000
Austria	5	250,000
Germany	4	200,000
Italy	3	150,000
Spain	3	100,000
Russia	1	100,000
Sweden	1	
		2,600,000

Good briquettes ought not to weigh above 22 lb., and should possess the firmness of natural coals. To attain this, they must contain at least 5 per cent. of pitch, if very strongly pressed, or 7 to 8 per cent. if made with less pressure. They must not leave more than from 6·5 to 6·75 per cent. of ash, if intended for locomotive use, or 10 per cent. if for steamboat use. Their regular parallelopiped shape permits easy stowage in the bunkers. The loss in transit by disintegration is only 1 or 2 per cent., against 30 to 50 per cent.

in the case of coals. They ought not to fall to pieces in the fire. Good patent fuel has 10 per cent. more heating-power than good steam-coal; it makes much less dirt, and, if manufactured with hard pitch, less black smoke than most descriptions of coal. One very important advantage of patent fuel is, that the fireman knows exactly how many pieces he has to put into the furnace at certain intervals in order to produce a certain effect, and that the foreman or manager can estimate whether this has been done by a single glance at the briquettes stacked beside the furnace.

The following notes on the development of this industry are mainly based on a prize essay by Berg*. Its principal seat is in Belgium and France. In the former country there are 8 or 10, in the latter 30 works. In England there are works at Swansea, Cardiff, near London, and near Newcastle-on-Tyne†. In Germany there are only two factories. Of the different processes, that of Baroulier (adding to coal-dust some bituminous caking-coal, pressing and heating in separate vessels) has not been successful, being too expensive and not yielding a product capable of bearing a long transit. Not much more successful have been a number of agglomerating substances successively proposed, such as vegetable and animal fats and oils, soap, gelatinous substances (glue &c.), mucilaginous decoctions of roots or whole plants, resins, magnesia cement, Carragheen moss, and wood-pulp. The only substances in general use are coal-tar [not used now] and soft and hard pitch. Soft pitch, mostly used in France, is melted in suitable pans, and mixed with the coals in the liquid state: hard pitch, mostly used in Belgium‡, is mixed with the coal in the state of powder, and the mixture softened by means of steam superheated to 300°; or else it is heated by direct fire, either in a hearth provided with a horizontal agitator (Chauselle), or in a revolving circular hearth with vertical agitator (Biétrix). With this plan, $4\frac{1}{2}$ per cent. of pitch is said to suffice. The coal is best if dressed, in order to free it from impurities, and then mixed with dry coal-dust to facilitate the pressing. There are presses with closed and

* Zeitschr. für Berg-, Hütten- und Salinenwesen, 1880, p. 148.

† This is erroneous; the patent-fuel works near the last-mentioned place were given up many years ago.

‡ According to information received by me from other sources, it would seem that the opposite is the case, viz. that more hard pitch is used in France, more soft pitch in Belgium.

others with open moulds, the latter either with direct or indirect action. In Mazeline's direct-action press the steam-cylinder piston on rising forces, by means of a one-armed lever, the press-ram from below into the moulds, which are contained in a circular platform, revolving by means of a ratchet. The finished briquettes are forced out by the rams sliding along an inclined plane. The ratchet arrangement is liable to frequent breakages. In the indirectly acting machine of Middleton and Detowbay the pressure is caused by an angle-lever carried down by a weight; the finished briquette is forced out by a second angle-lever. Here also the platform is turned round by a ratchet arrangement. In the similar machine of Hanrez, the lever presses at the same time from above and below, limited by a hydraulic ram, the forcing-out is effected by an inclined plane, the revolution of the platform by a ratchet. In Durand and Marsais's machine (especially adapted for smaller work) the ram is pressed into the mould by an eccentric sheave, afterwards by a similar sheave the closing-plate is removed and the briquette pushed out. Another similar machine has been constructed by Biétrix.

In the case of machines with open moulds, the pressure is obtained by the friction of the mass at the conical mouth of the press. Hence they require more power than those just described, but do more work; they are as yet employed exclusively with soft pitch*.

In the most widely-used machine of this kind (Evrard's) the tubular moulds are arranged radially in a circle, so that the eccentric attached to the vertical working shaft can by turns force the rams in and out of the moulds. At every back stroke of the ram a fresh mass is forced into the mould, which by the forward stroke is pressed against the old mass and forces this out of the open end of the mould. A similar machine, by Bouriez, permits the use of hard pitch also. Revollier's and Mazeline's machines are worked by hydraulic pressure.

Of recent patents for manufacturing patent fuel we will mention:—E. F. Fiedler (G. P. 16,017, of 1881); G. H. Lenk and W. H.

* The latter process is quite analogous to that of moulding bricks—the machines that work with dry clay being constructed with closed moulds, those for wet clay with conical mouthpieces (dies). But it is well known that the former take much more power and have a much larger output than the latter. Is the opposite really the case with patent-fuel presses?

Lehmann (G. P. 15,789, 1881); G. J. P. Couffinhal (G. P. 15,239, 1881); M. Neuhaus and O. Henniges (G. P. 18,538, 1881); S. Butler (B. P. 7791, 1886).

Bornemisza and Kopal (G. P. 31,664) made a kind of artificial fuel by mixing with 100 parts of melted coal-tar pitch wood-cuttings or other vegetable refuse, allowing to cool down on stone slabs, moulding into pieces 4 × 2 × inches, with a central hole, coking these pieces, puting on an iron rod, within a wire-gauge cylinder contained in an ordinary gas-retort, and pressing the product once more while still hot.

Varnishes made with Pitch, Refined Tar.

A very rational employment of coal-tar pitch is for making varnishes, for iron especially, but also for wood &c., of course all of them black. They are all made in a very simple way, by melting pitch with various products of tar-distillation, and hence require no introduction of any foreign matter. No plant is required, but an open pan, set in a covered place, so as to be heated from without; but it is certainly preferable to employ a closed pan with a mechanical agitator. The melting-pan may be made either of cast or wrought iron; but it is best if made of the latter, because then no cracking (very dangerous in this case!) can occur. It may be an upright cylinder with convex bottom, or a horizontal boiler. For working on a large scale a mixing-apparatus like that represented in fig. 78, p. 272, is preferable.

In this pan the whole quantity of pitch to be worked up is melted along with a little of the oil to be employed, which promotes the melting of the pitch and prevents its speedy solidification. Still the temperature will rise pretty high before all the pitch is melted, and it is best to let it cool down a little, lest the oils now added should be raised to the boiling-point, which will of course most readily happen with light oil or naphtha. But the cooling must never be allowed to go so far that some part of the mass begins to solidify. Now the remainder of the oil is added quite gradually, stirring each portion completely into the mass. From time to time a sample is taken out and cooled, to see whether the proper consistency has been attained.

The commonest kind of varnish is made in the manner just described, from pitch and creosote oil. In this case even a simpler process may be followed. The tar is distilled (if need be, in a

separate small still) till the light oil has passed and heavy oil begins to pass, or till all the "middle oil" has passed over, say up to 240°. The fire is now drawn out, the still allowed to cool down a little, and the residue ("asphalt"), diluted within the still itself with the necessary quantity of creosote oil, say ¼ of the weight of the pitch, after which it is run off in the liquid state. Or else the distillation is carried on to hard pitch, in order to obtain the anthracene; the heavy oil, freed from anthracene and, if possible, from naphthalene, is run in till the necessary degree of thinness is attained; and the mass is well mixed. We have described this process above, pp. 243 & 246, as it is carried out within the stills themselves; but sometimes the creosote oil is mixed with the hard pitch in the pitch-cooler, a pipe conducting it from a store tank into the fluid pitch within the cooler. The varnish thus obtained, in England called "refined tar," in Germany known as "prepared tar" or "artificial Stockholm tar," is less valuable to the tar-distiller than raw tar, since the more valuable components—benzol, phenol, anthracene, and partly naphthalene—have been removed; on the other hand, it is much more valuable than raw tar for many purposes—as a paint, for the manufacture of roofing-felt, for roperies, &c. It penetrates much more quickly and deeply into wood, stone, &c. than raw or even boiled coal-tar, and dries much more quickly, even more so than wood-tar (real Stockholm tar). It is greatly to be recommended for alkali and other chemical works, for painting any wood-, iron-, or stone-work needing protection against acids, chlorine, &c. Such prepared tar is especially very much to be preferred to boiled tar for painting iron (where raw tar, owing to its ammonia, is quite inadmissible), as it dries both much more quickly and without leaving cracks, and forms a good, shining coat. The drying takes from 12 to 24 hours, according to the weather. As this sort of varnish forms a pretty thick coat, it is only applicable to coarse ironwork, but is excellent for this.

A better kind of varnish is obtained by melting pitch with light oil in the above-described manner. For this purpose, not the light oil distilled from the tar, but the last fraction from the light-oil [illegible] oil taken away from the carbolate of soda (compare [illegible] is employed, which is deprived of its more valuable [illegible] By 100 parts of moderately hard pitch about 60 [illegible] light oil may be calculated. This varnish gives a more

lustrous and smooth surface than the former, and leaves a much thinner coat. Its drying-time varies from four to six hours; and it can be employed for finer ironwork.

Lastly, more quickly-drying and thinner varnishes can be obtained in all gradations, by substituting naphtha for part of the light oil, either the commonest burning-naphtha being employed or else some made on purpose by carrying on the rectification by steam (Chap. XI.) beyond the usual termination. The rule is, first to work up all the light oil with the pitch, and then to add the naphtha, keeping the mixture as hot as is consistent with the volatility of the naphtha. Besides, very thorough and long-continued stirring is necessary, since naphtha is not so easily incorporated with the varnish as the heavier oils, and the varnish would otherwise be very likely to separate into a black deposit with naphtha floating on the top of it. It is possible by means of very common naphtha to make varnishes drying in an hour, or even in a quarter of an hour, which can be employed for any kind of hardware where its blackness is of no consequence. In lieu of coal-tar naphtha, petroleum spirit &c. can be employed.

All three kinds of varnish adhere firmly to iron, and after drying exhibit a considerable degree of hardness, together with glossy lustre and smoothness, and more of the latter in the case of the better descriptions.

A patent of Marchisis and Stevens (23rd Sept. 1870) seeks to improve such varnishes by heating with bleaching-powder or a solution of common salt, and washing with copperas solution. Whether this does any good we cannot tell.

Chaumont* makes a varnish for wood and metals by dissolving 300 parts of coal-tar asphalt in 100 carbon bisulphide. In lieu of such asphalt, natural bitumen or resin may be employed. The materials are brought together in a closed vessel, to prevent the evaporation of the carbon bisulphide. In 12 to 24 hours the varnish (the smell of which will hardly recommend it) is ready for use.

Watson Smith† recommends as a good varnish for tarpaulins one obtained by melting wood-tar pitch with the same weight of coal-tar creosote oil, freed as much as possible from naphthalene; also as a good metal-varnish one obtained by melting 6 lb. of

* Wagner's Jahresb. 1865, p. 686.

† Private communication.

dark rosin with a pint of boiled linseed oil and a gallon of creosote oil, to be mixed, for finer work, with a little gum and any kind of colouring-matters.

E. Heusser (G. P. 24,231) extracts pitch with warm light tar-oil or benzoline. A solution is formed which, on evaporation, leaves a mass resembling native asphaltum. The residue left after extraction forms a black paint of great covering-power.

Asphalt, Asphalt-paper, Roofing-felt, &c.

Asphalt, both that obtained directly in the distillation of coal-tar, and that made by mixing pitch with heavy oils and with solid substances, is a substance of manifold uses. It is employed for keeping off the subsoil moisture from metal pipes, iron tanks, &c. sunk in the ground. For this purpose the semiliquid mass is mixed with sand, ashes, &c. into a lumpy paste, of which a thickness of 4 or 6 inches is employed. We shall quote particulars of such mixtures below.

Such asphalt, made direct from tar, is not used now so frequently as formerly; but similar mixtures are artificially made, by driving off all the creosote and anthracene oil, and pumping back the heavy oils, meanwhile freed from their more valuable components, as phenol and anthracene, till the desired consistency of the residue has been attained. Thus is obtained not merely soft pitch, but also asphalt, and, with greater dilution, even "refined tar" or "artificial Stockholm tar," which is especially largely employed in the manufacture of roofing-felt (see below).

The employment of pitch or asphalt for *street-paving* is to be recommended in many respects. When used as a cement for joining the paving-stones, it makes the ground impermeable to the impurities from below and does not permit the passage of noxious effluvia. Tar-pitch is also used as a direct *substitute for natural asphalt*, but only in combination with the latter, for asphalting footpaths, and for insulating foundation-walls from the ground-moisture. The mixture is melted in pans in the usual way; sand, brick-dust, ashes, chalk, and the like are added till the mass has become thick enough (for which purpose about four times the weight of the pitch will be necessary); the whole is well mixed up, preferably by grinding in a pug-mill, and used hot. For foot-paths the pitch is ground up with an equal weight of sandy or

stony material, melted in a pan, and, before being laid down, is mixed with an equal quantity of gravel; so that the finished pavement contains about 30 per cent. of pitch. But it is not advisable to employ coal-tar pitch alone, without any natural bitumen; the latter is much more intimately combined with the earthy matters than the former can be. A mixture of the two is very suitable, and is cheaper than natural asphalt alone. In a similar way, moulded blocks are made from pitch and ground rock.

At some Scotch tar-works the pitch is run directly from the tar-still into a pug-mill, where it is intimately mixed up with sand, sometimes also with chalk. From this mill, while still liquid, the mixture is run off into sand moulds to solidify. During the whole process, until the completed asphalt becomes cool, offensive vapours are given off; the pug-mill or mixing-pan ought therefore to be covered with a hood, and the vapours carried away into a chimney-stack by means of a pipe. The space between the edge of the hood and the mill or pan should be enclosed by sacking which can be opened at certain places as requisite for manipulation. (Dr. Ballard.)

Gobin (B. P. No. 1865, May 9, 1878) melts 15 parts of bituminous shale with 35 parts of coal-tar pitch in a pan, till the froth which at first arises has subsided. Then he adds 10 parts of coke and 130 of limestone, both crushed, well mixed, and dehydrated by heating above 100°. Before cooling he adds another 160 parts of gravel, well dried by heat. For street-pavements he increases the quantity of gravel up to 190 parts, moulds the mass into blocks of about $8 \times 6 \times 4$ inches, and lays these, like ordinary paving-stones, on a bed of gravel or sand.

Daguzan (Germ. patent 4999) mixes tar, first completely dehydrated by heat (probably he means "asphalt"), with previously "calcined," finely ground limestone or marble (quicklime?), 5 per cent. oxide of iron, potassium silicate, calcium sulphate, &c.

Thenius* proposes mixing soft pitch with 10 per cent. of rosin oil, which is to make it more like natural asphalt, or with 50–60 per cent. of crushed limestone. This mixture is moulded into blocks, and is, with the addition of 25 per cent. of ground gravel or basalt, cast into mosaic plates for pavements, tables, &c.

* Technische Verwendung des Steinkohlentheers, p. 117 *et seq.*

Tar asphalt can be considerably improved by the addition of *brimstone*. A. Winkler* adds to coal-tar asphalt (in the sense of the term adopted in this chapter) 5 per cent. of brimstone in small quantities, heating the mixture every time till no more sulphuretted hydrogen is given off. Probably, in the heating, the sulphur decomposes the components rich in hydrogen, and thus renders the residue less fusible. Thus 75 per cent. of the tar is obtained as good asphalt, which does not soften in boiling water. A further proposal of his does not seem practicable, viz. to add 20 per cent. of brimstone to the tar before distillation; it is said that in that case only water and sulphuretted hydrogen escape during the heating, and good asphalt is obtained, equal in weight to the tar employed. The expense, the action of the sulphur on the metal of the stills, and the nuisance caused by the sulphuretted hydrogen would be objections. A similar mixture is *Häusler's wood-cement*, well known in Germany as a roof-covering. This kind of roof has been very much employed of late in Germany and Switzerland as being practically fireproof, a bad conductor of heat, and almost indestructible.

Coal-tar asphalt, or very soft pitch, is also employed for manufacturing *asphalt pipes*. This industry, introduced by Jalourean, has been minutely described by Behrens†. Endless hemp paper, 7 feet wide, is passed through a semicylindrical pan set in a furnace and filled with hot pitch‡. A roller revolving in the pan takes up the paper soaked with pitch and conveys it to a smaller roller, forming the core of the pipe, round which about 100 layers of paper are wound. When the proper thickness has been obtained, fine sand is dusted on, and the whole is exposed to considerable pressure, which increases the compactness and homogeneity of the mass. After a short cooling in water, the core (which had previously been rubbed with soft soap) is drawn out by means of a crane, and the pipe is once more cooled by water. The joints of the pipes are made by iron flanges put upon them, or by thimbles formed of a wider piece of asphalt piping, and fixed on the pipe by a mixture of pitch and brimstone, or else by winding round them

* Chem. Centralblatt, 1858, p. 337. † Dingler's Journ. ccviii. p. 377.

‡ That Behrens does not mean real pitch, but either asphalt or very soft pitch, is apparent from the fact that paper would be partially destroyed at the melting-temperature of hard pitch.

ten or twelve folds of linen cloth soaked in melted pitch. Similarly any necessary elbow-pieces and bends are made, often at the place where the pipes are laid down.

According to the nature of the pitch employed, the pipes have different qualities, which must be taken into account in using them. If made with very soft, oily pitch, the pipes offer great resistance to the penetration of water, and hence are excellent for water-pipes in marshy ground. Those made of harder pitch offer a greater resistance to deformation by a higher temperature. Of course asphalt pipes can only be employed for conveying cold liquids or gases; but, with this restriction, they can be used for many purposes, both on account of their relatively low price and their valuable qualities. They resist a pressure of 33 atmospheres from within [?], and are elastic enough for their joints not to break in case the ground settles down; they are not subject to be frozen up, being bad conductors of heat; they are not acted upon by dilute acids or alkalies, and can be laid in any soil. They are chiefly employed for conveying water, acids, air-blasts, for pit-ventilation, for covering underground telegraph-wires, for speaking-tubes, and sometimes for gas-pipes.

Such asphalt pipes and semicircular spouts made by cutting them in halves are excellent for carrying away waste liquors of an acid nature in chemical laboratories, and even in chemical factories, so long as they are not exposed to any heat.

Another kind of pipes are made from (probably harder) pitch by mixing it with gravel and casting it in moulds over a core of thin sheet-iron; the outside is covered with gravel, which is pressed or rolled in while the mass is still warm. The walls of these tubes must be very thick, as they are brittle. These pipes, manufactured by Chameroy, are very much employed in Paris as water-pipes.

When any kind of asphalt tubes are used, it must never be forgotten that they are liable to be deformed by heat.

Behrens (*loc. cit.*) also describes the manufacture of *asphalt paper* as a substitute for wax-paper. Ordinary wrapping-paper is wound off from a roller upon a heated drum, upon which a scraper is fixed. Melted pitch runs down in front of this to a depth of 1½ inch. The paper thus covered with a thin film of asphalt runs over several rollers, and is ultimately wound round the last. Another kind of paper, consisting of a thin layer of pitch between two layers of

paper, which is much used for papering damp walls, is made in a similar manner.

One of the most important uses of a sort of asphalt paper is that for *roofing-felt* or *roofing-paper*. We have already mentioned this industry when speaking of the applications of coal-tar without distillation (p. 163), but we have also pointed out that it is the most rational proceeding to separate from the coal-tar its most volatile constituents—benzol, carbolic acid, naphthalene, and anthracene, and to prepare from the residual distillates, that is most of the heavy oils, along with the pitch, a mixture of the proper quantities for the present purpose. We have, in fact, already described such mixtures as "varnishes" and "refined tar;" "asphalt" is only another such mixture; no sharp distinction can be drawn between all these products.

Probably most of the roofing-paper now manufactured both in Germany and the United States is made from "refined tar," as described p. 163. In the United States, where there is no outlet for pitch for manufacturing patent fuel (comp. p. 15), most of it is used up in the just-described manner for making two- and three-ply roofing-paper. The latter is used both as a cover by itself, with the usual coating of tar and sand, and for "gravel roofs." The latter are made by laying on an ordinary tar-paper roof a coating of hot medium pitch, and covering the whole with a layer of gravel. This is very similar to the way in which Häusler's wood-cement (p. 282) is used; but the latter is laid, in the fused state, on ordinary coarse paper, and three layers of this, alternating with wood-cement, are followed directly by a layer of gravel.

It is sometimes asserted that the roofing-paper made with "asphalt" or "refined tar" is more greasy and less durable than that made with raw tar; but most probably this is only a question of "refined tar" of proper quality.

The Distillation of Pitch.

Long before the technical importance of anthracene had been recognized, attempts had been made to obtain further products from the pitch left behind after the distillation of coal-tar. The occasion for those attempts was the fact that coal-tar pitch was not consumed in any large quantity, except for patent fuel, and that with only this

single opening the sale of the article would be very liable to stoppage. The idea of carrying on the distillation till all the volatile products were given off and only coke remained (for which there was always a certain sale) was very plausible. The motive for doing so became much stronger as soon as the discovery of artificial alizarin had raised anthracene to the rank of the most valuable component of coal-tar. It was known that the pitch contains much anthracene; and the hope of obtaining it therefrom at a profit seemed justified.

The apparently simplest plan, that of carrying on the process in the tar-still itself to the stage of coke, is not feasible. We have seen on p. 200 that cast iron is not well adapted for tar-distilling, and wrought iron would be burnt away too quickly. Moreover, cutting out the coke would be very costly and would enormously injure the iron plates. A method proposed by Puls (patented August 23,1858, No. 1910), viz. adding earthy substances to the tar, so as to prevent the red-hot residue from adhering to the still, would cause the loss of the coke, and is not worthy of serious consideration.

Hence distilling the tar up to pitch in the ordinary stills, and distilling the pitch in separate vessels, either charging them with it in the solid state, or running it while still liquid into the pitch-oven, cannot be avoided. This may be a brickwork muffle, or a fire-clay gas-retort, or an iron vessel of some shape or other.

The *brick pitch-ovens*, which were formerly sometimes employed*, will be but briefly mentioned here, as they have not proved practically successful. They were muffle-furnaces, about 15 feet long, 6 feet wide, and 6 feet high to the crown of the arch, fired by zigzag flues running underneath the concave-shaped furnace-bed. At each gable-end there was a working-hole, about halfway up, closed during the process. The vapours were carried away by a cast-iron pipe, 90 feet long, and were condensed by air-cooling. Usually two ovens were built side by side, each was charged with 2 tons of pitch, the doors closed with metal plates fastened like gas-retort-covers and screwed down. The fire having been lighted previously, volatile products were soon formed, which were con-

* Figured and described in Ronald and Richardson's 'Chemical Technology,' i. p. 541.

densed in the cooling-pipe and collected in a tank. The oil first coming over resembled the last distillates from coal-tar; the following portions were more viscid, very dark and empyreumatic. After about twelve hours, when the distillation was nearly finished, large quantities of heavy yellow vapours appeared, condensing partly to a very thick pasty mass; sometimes they yielded a reddish-yellow pulverulent substance, which on exposure to the air soon turned soft and sticky, and contained much pyrene, chrysene, and other hydrocarbons. When nothing more came over, the two gable-end doors were cautiously opened; the vapours inside the muffle took fire, and the soot adhering to the sides and the arch was burnt. The dense smoke then issuing from the doors was aspirated by a vapour-hood and conveyed to a chimney. The cold current of air caused the layer of coke on the furnace-bed to crack and break up into pieces, the attendant using iron tools to accelerate the process. The coke was drawn out red-hot and quenched with water. It was quite honeycombed, owing to the escape of vapours from the pasty mass. The heat produced by the burning of the soot kept the oven red-hot, so that very little fuel was required to be used for the next operation. One hundred parts of pitch yielded 25 parts of oil, which could be mixed with the creosote oil or sold as a common lubricant, and 50 parts of coke; 25 parts were lost. But these were *maximum* yields; in practice very much pitch was lost by leaking through the brickwork, and hence the yield was smaller than from the iron retorts.

Of newer statements upon this subject, dating after the invention of alizarin, we shall first quote a report made by Behrens*, upon experiments made by him on a large scale. He employed a cast-iron retort in the shape of a horizontal box 13 feet long, 3 feet 8 inches wide, and 3 feet 8 inches high, constructed of 16 flanged plates, bolted together and joined by rust cement. The front and back openings were closed by iron doors, and luted with lime-putty. On the top of the retort there was a man-hole for charging with solid pitch, and a cock for charging with liquid pitch, and also a safety-valve and a 6-inch pipe for the vapours. The latter was connected with an iron box provided below with a swan neck pipe to run off any liquid, and on the top with a pipe for carrying away steam and uncondensed vapours into a condensing-worm. The retort was set on a flat arch, which was levelled above

* Dingler's Journal, ccviii. p. 371.

and heated from below by a fireplace in front; at the back the flame divided into two parts, returned, through two lower flues on each side of the retort, to the front, and once more, through two upper side flues, to the back. At first a little water comes over, especially with damp pitch, and hence cautious firing is necessary to prevent boiling over. But as soon as the pitch is fairly boiling, oily matters condense, and the distillation goes on rapidly even with moderate firing, so that 3 tons of pitch can be distilled in 3 or 4 hours and yield 14 or 15 cwt. of oils. The latter are condensed in two fractions—the first as anthracene oil, the second as lubricating-oils. From the beginning, with these arrive water, gases (especially ammonia* and hydrogen), benzene, naphthalene, and volatile oils (of sp. gr. 0·97). When two thirds of the oil have distilled, the formation of coke commences; the mass swells; and if the retort has been fully charged, the fire must now be slackened.

When the production of oil is near its close, the more volatile hydrocarbons decrease, but there is even more steam and gases. At last there comes a reddish-yellow resinous sublimate, which gradually ceases; and the evolution of gases ceases also. The retort is now carefully opened, and the gas issuing from it is lighted; otherwise the access of air might cause an explosion. There were obtained:—

Oils containing anthracene.....	27–30 per cent.
„ „ chrysene and pyrene	
Sublimed reddish-yellow rosin	
Coke.....	48–52 „ „
Gases, steam, and 0·2 per cent. light oils...	25–28 „ „

The crude anthracene oil, on treatment with alkalies, yielded 3 per cent. of an oil soluble in alkalies, and separated again by sulphuric acid, which on distillation gave 8 per cent. of water, then more and more viscid oils, and, above 360°, a transparent wine-coloured solid mass; a little carbon remained behind.

The following apparatus of Fenner and Versmann for coking pitch has been worked on a large scale. The tar is first distilled in an ordinary wrought-iron still; that shown here (A, fig. 79) is shaped like a horizontal boiler. B is the condenser for light oils

* Watson Smith also has observed the evolution of ammonia in the coking of pitch (Journ. Chem. Soc. 1884, pp. 144–148).

and creosote oil. When the anthracene oil is about to come over, the liquid pitch is run, while still hot, into a series of cast-iron vessels C C C, in which the coking is effected. It passes through

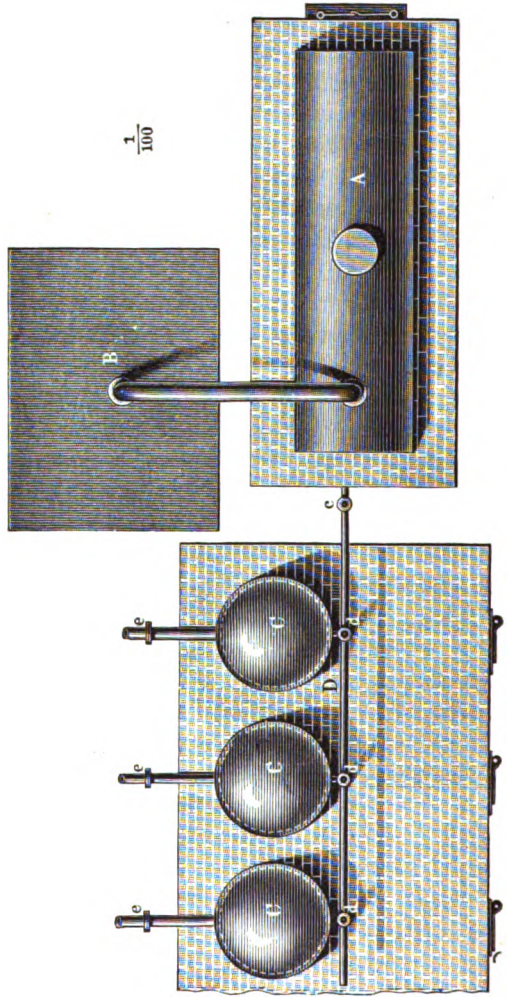


Fig. 79.

the cock *c*, the main pipe D, and the taps *d d d*, into each of the pitch-stills. Figs. 80 and 81 give details of the latter. They are made of cast iron, and are about 4 feet in diameter, and 4 feet 8 inches deep (inside measurement); it is alleged that, when set

in the way indicated in the diagram, they will last five or six years, distilling off one charge of 1½ to 2 tons of pitch every

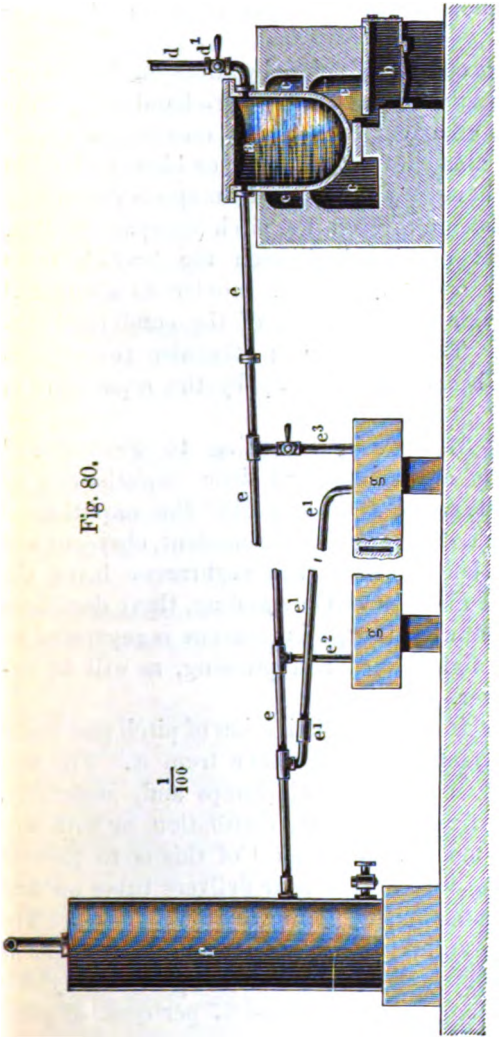


Fig. 80.

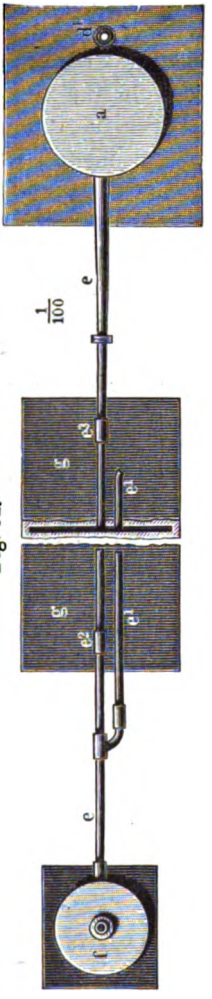


Fig. 81.

three days—one day being occupied in the distillation, and two more in the cooling, emptying, and recharging. A production of 10 tons of pitch per day therefore requires three sets of six cast-iron

pots each for the coking-operations. *a* is the cast-iron pitch-still; *b*, furnace; *c c c c*, flues; *d*, pitch-delivery pipe; d^1, stopcock; *e*, condensing-tube for the vapours evolved; e^1 e^2 e^3, branch pipes delivering condensed liquors to the tank; *f*, condensing-chamber; *g*, tank.

The vapours evolved are condensed solely by atmospheric cooling, partly in the tube *e*, partly in the condensing-chamber *f*. The evolution of vapours is greatly facilitated by creating a partial vacuum in the pot *a* by means of an exhauster or blower attached to the exit-pipe of the chamber *f*; but no advantage is derived by blowing either hot air or steam through the pitch (compare p. 238). Towards the latter part of the distillation the branch tubes e^1, e^2, e^3 are successively opened, so as to provide as short and ready a passage as possible for the escape of the condensed substances into the tank *g*. This is essential; otherwise the vapour-delivery-pipe *e* is apt to become blocked up by the separation of solid matter.

The distillate of 315°–370° C. is, according to Fenner and Versmann, very rich in anthracene, but little naphthalene or chrysene are present; between 260° and 315° the naphthalene is in excess; above 370° anthracene is less abundant, chrysene and other bodies of higher boiling-point than anthracene being the main constituents of the distillate. On standing, these distillates deposit solid matter, from which rough anthracene is separated by filtration, washing with lighter oils, and pressing, as will be described in the next chapter.

This plant may also be used for the distillation of pitch purchased in that state for the extraction of anthracene from it. For this purpose the pitch is broken up into small lumps and, preferably, mixed with oils arising from a previous distillation, or with dry absorbent carbonaceous matter. The object of this is to prevent frothing and the blocking-up of the vapour-delivery tubes on first heating, owing to the presence of moisture in the pitch. The patentees state that, on an average, 2 per cent. of anthracene is thus obtainable from ordinary pitch. As ordinary coal-tar yields about 0·5 per cent. of rough anthracene, and 67 per cent. of pitch (this latter corresponding to 1·33 anthracene per 100 of original tar), it follows that the production of anthracene is nearly quadrupled when the tar is coked; *i. e.*, all together, 1·85 per cent is obtained instead of 0·5 per cent., if the above statement be correct.

Unfortunately "pitch-anthracene" has been found so much contaminated with chrysene &c. that the alizarin-manufacturers cannot very well purify it, and will not work with it at any price. Several lawsuits have arisen from this circumstance, and the manufacture of pitch-anthracene seems to have been given up entirely now. It could hardly be otherwise, as the production of dorinary anthracene in the United Kingdom alone is in excess of the present demand of the whole world (see next chapter). The coke left behind is very good (see below); and the oil from which the anthracene is separated is a good lubricator; this is actually the only opening for the pitch-oils in general, until some better method of purifying the pitch-anthracene be discovered.

Watson Smith * obtained from ordinary hard pitch by distilling, mixing the distillate with mother oils and redistilling, no more than 0·556 per cent. rough anthracene from the pitch, or 0·33 from the tar.

The proposal of E. Kopp (p. 237) might be referred to this chapter also.

It is asserted that since the introduction of steam in the last stage of tar-distilling all the anthracene is taken out of the pitch, and that it is thus from the outset impossible to work the pitch for anthracene, as there is none in it; but I am not aware of any direct proof for this opinion, and do not share it.

The *coke* obtained by distilling pitch is very good if properly made, but only in that case. This matter has been treated in detail by Behrens (*loc. cit.*). The quality of the coke depends upon the temperature at which it has been made, and upon the length of time during which it has been exposed to that temperature. If both are insufficient, a dull, blackish, compact mass is obtained, with but few cracks. On opening the retort this coke takes fire and burns with a luminous flame issuing through the cracks of the mass. Even though the coking is somewhat promoted by such burning out, and the cracks are widened with a crowbar, the quality of the product is very inferior, owing to all pitch-coke, except the very hard-burnt kind, crumbling to dust in the fire. Hence coke that is only burnt out afterwards

* Private communication.

possesses but very little cohesion; and as it strongly adheres to the sides of the retort, much dust is produced in breaking it up and getting it out. Coke not ignited, having been quenched with water, must from time to time be drenched with water again, as otherwise it easily takes fire. In order to make *hard* coke, the temperature inside the retort, when the red vapours indicating the end of the distillation have disappeared, must be brought to a bright red heat; and this should be kept up for eight hours at least. Thus a complete operation lasts about 24 hours. Hard-burnt coke adheres but little to the sides of the retort, possesses great cohesion, and consists of prismatic columnar pieces, which can be got out of the retort almost without using a crowbar. After being once quenched it does not take fire again. It is light grey, very dense, and does not crumble in the fire. Behrens made some experiments with such coke in English iron-works, with the following results. No success was attained in employing it for melting cast iron in cupolas in lieu of charcoal, or for refining wrought iron on hearths; in the latter case the slag was not easily separated from the iron. But hard pitch-coke is very good for refining pig-iron in the English way, which is usually done by gas-coke; the refined pig afterwards yielded very good wrought iron on puddling. This coke is also very well adapted for fusion processes in crucibles.

According to Staveley *, pitch-coke contains only 0·11–0·12 per cent. sulphur and 2·43–2·50 per cent. ashes; it does not crumble even when exposed for months in the open air, as there is no sulphide of iron in it; and it surpasses even the best Durham coke in hardness, density, heating-power, and strength to sustain heavy loads.

One of the principal difficulties in the distillation of coal-tar pitch, which prevents this operation from being very extensively carried out, is that of finding a suitable material for the retorts. Brick muffle-furnaces leak too much; fireclay retorts require too much fuel in proportion to the quantity of pitch worked up; cast iron is quickly destroyed by the heat and the pitch, although Fenner and Versmann assert the contrary respecting their construction figured above.

Cyrus M. Warren (German patent No. 12933, July 16, 1880)

* Chem. News, xliii. p. 228.

proposes distilling tar as usual down to hard pitch, then running into the still whilst hot residues from petroleum-refining, and distilling off once more as much of the oils as corresponds to the weight of the petroleum-residues. From this oil anthracene separates, together with paraffin, which latter is removed by hot-pressing. (It is doubtful whether this plan will furnish very saleable anthracene; nothing is more dreaded by the manufacturers of alizarin than the presence of paraffin in their anthracene.)

More rational would appear the proposal of Wischin (Engl. pat. 1980, 1880), to add gradually, at the last stage of tar-distillation, heavy coal-tar oil, preferably heated beforehand, whose vapours carry away the anthracene without injuring the quality of the pitch.

An attempt made by Behrens (*loc. cit.*) to employ the pitch in *gas-making*, by melting it and running it through a bright-red iron tube, yielded, on an average, for 1 kilog. pitch, 250 litres of gas, but almost devoid of illuminating-power. It consists mainly of hydrogen, and contains some sulphur, and would therefore be hardly of any value in gas-making.

Balfour and Lane (B. P. 12721, 1886) add from 5 to 10 per cent. of soft pitch to the coal used in the manufacture of illuminating-gas, in order to get more and better gas, richer in benzene, and denser coke, containing little sulphur. The improvement in the quality of gas would seem to be very doubtful.

When pitch cannot be utilized in any other manner, it can be *burned to lampblack*. The furnaces and condensing-chambers for this purpose are similar to those described on p. 165 for burning tar. Only, as the pitch is solid, it must from time to time be thrown upon the red-hot iron plates on which it is to be burnt. No doubt a vessel might be fixed above this, where the pitch would be melted by the combustion going on below, and from which it would be run out continuously by means of a valve in the bottom. According to Thenius 500 kilog. of pitch yield 200 of different descriptions of lampblack, and 200 kilog. of coked residue, which is knocked off with hammer and crowbar and used as fuel. Along with pitch any dry alkaline residues from purifying the tar-oils may be burned; but usually none are obtained, as the alkali is employed in aqueous solution.

Testing of Pitch.

Pitch is usually tested for its softening or melting-point.

Soft pitch (*brai gras*) softens at	40°,	melts at	60°.
Moderately hard pitch	„	60°,	„	100°.
Hard pitch (*brai sec*)	„	100°,	„	150°–200°.

A practical test is kneading a sample between the teeth. If this can be done easily, the pitch is soft; if with more difficulty, it is moderately hard; and if it is crushed to powder, it is hard. Soft pitch is more shining and black than the very hard pitch, which verges upon grey and has less lustre. Sometimes the latter is even a little porous; if it is more so, it is partly coked and cannot be used for patent fuel. The specific gravity of hard pitch is about 1·3.

A test for soft pitch, to see whether it is suitable for patent fuel, is dipping a piece of about 4 inches length and ½ inch diameter for 2 minutes in water of 60°; when taken out it ought to bend without breaking. For harder descriptions water of 70° is taken; on the other hand, it is sometimes required that pitch should easily twist at 55°.

I am indebted to Mr. F. G. Holmes, of Messrs. Burt, Boulton, and Haywood, for the following notes on a method for testing pitch (softening and fusing-point) :—

"Several pieces of pitch are taken from different parts of the sample and cut to the size of a half-inch cube. These cubes are then fixed on metal wires by heating the ends of the wires and pressing them into the pieces of pitch, which are then suspended in a vessel containing about 500 cub. centim. of water heated by any convenient means, at a uniform rate of 5° C. per minute, as indicated by a thermometer immersed in the water with the bulb about 1½ to 2 inches from the bottom of the vessel.

"The cubes are suspended on a level with the bulb of the thermometer. As the temperature rises the pieces of pitch are taken out from time to time and twisted or squeezed with the fingers, and the temperature noted at which they assume the following conditions :—

(1) Readily twisting or soft.
(2) Very soft.
(3) Fused.

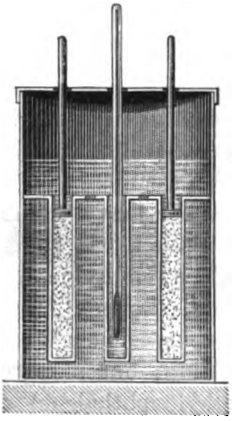
(1) The twisting-point is when the pitch can be easily twisted round several times.

(2) Very soft, when it yields to a very light pressure of the fingers.

(3) Fusion, when the pitch melts off the wire."

More accurate results are obtained by the following contrivance (originated in France, and also communicated by Mr. Holmes). The tin cylinder, fig. 82, contains a horizontal partition, in which five tubes are inserted, closed at the bottom. The central tube serves for introducing a thermometer, the other four tubes are filled with ground-up and sifted pitch. The sifting must remove both the coarse particles and the dust. The pitch-powder is weighted by an iron disk attached to a pin of definite weight, the perforations in the top-cover serving as guides for the pins and the thermometer. The cylinder is now filled with water a ittle above the tops of the tubes, and is heated over a lamp till the disks sink down into the melted pitch, the temperature being noted at that point.

Fig. 82.



Sometimes the *volatile matter* ("*bitumen*") in pitch is estimated. This is best done in the way usual for testing bituminous coal for the yield of coke, viz. by heating say 1 gram of finely powdered pitch in a platinum crucible of 1¼ to 1½ inch height, with the lid on, by means of a good Bunsen burner, first gently, till no more smoke and flames issue between the crucible and its lid, then as strongly as the burner will permit. The operation should last about twenty minutes. The crucible is placed in a desiccator and the coke is weighed after cooling; it amounts to from 25 to 50 per cent. of the pitch.

In order to estimate *fixed carbon* (coke-dust) in pitch, it is successively treated with hot benzene, carbon disulphide, and alcohol, and this treatment is once more repeated. The operation is conveniently carried out by means of a Soxhlet's extracting-apparatus.

CHAPTER VII.

ANTHRACENE OIL.

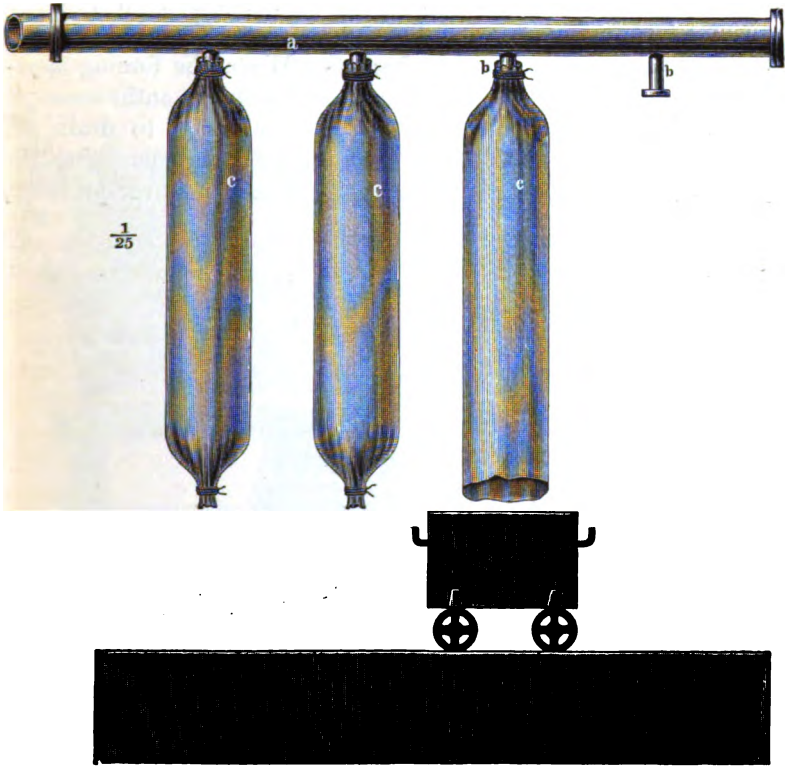
ANTHRACENE OIL (green oil, green grease, red oil) consists of the highest-boiling portions of coal-tar, starting from the point at which the oils begin to separate solids again (*i. e.* when the thermometer shows about 270° C. in the vapour) to the end of the distillation. It contains essentially the following bodies—naphthalene, methylnaphthalene, anthracene, phenanthrene, acenaphthene, diphenyl, methylanthracene, pyrene, chrysene, retene, fluorene, fluoranthene, chrysogen, benzerythrene, carbazol, acridine; but along with these substances, all of which (except methylnaphthalene) are solid and partly only fuse at a high temperature, there is a mixture of liquid, high-boiling oils of which we know as yet next to nothing. Substances containing oxygen (phenols of high boiling-point) are also present; of these α and β naphthol have been distinctly proved to exist in coal-tar. The whole forms a mass rather thinner than butter, with crystalline grains or scales mixed in, of greenish-yellow colour.

The working-up of anthracene oil consists essentially in the separation of the solid hydrocarbons from the liquid ones by cooling and pressing. The latter go back to the heavy oil, of which the anthracene oil was the last fraction; or they are employed as lubricants, or are redistilled. The solid portion is either sold as rough anthracene or is further purified by "washing."

Simple as the process of making rough anthracene looks, the different ways in which it is carried out make great differences in the yields of anthracene, which, from the high price of this article, very much affect the profits of tar-distilling.

The anthracene oils are sometimes separated in two fractions, apparently without much advantage. They are first allowed to rest for some time, so as to cool and deposit the crystallizable substances. Even in summer three to five days should suffice; but at some works a fortnight is allowed. In any case much anthracene remains dissolved in the liquid oils, which are therefore often redistilled in order to obtain more. Cooling by means of refrigerating machines hastens and completes the crystallization; but as it also renders the mother oils very viscid, artificial cooling would seem adapted only for the hot season. The cooling is best

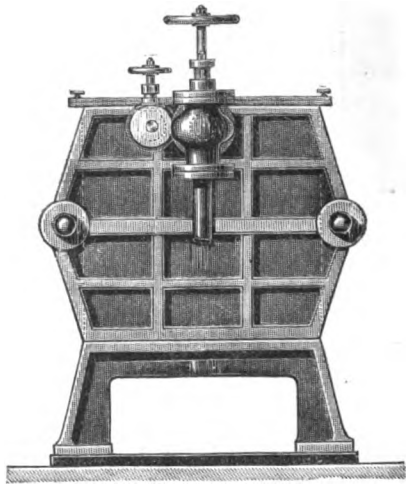
Fig. 83.



done in shallow iron pans, not above 18 inches deep; where space is an object, several such may be mounted on the top of one another.

When the crystallization is complete, the pasty mass, testing about 10 per cent. of pure anthracene, is forced by air-pressure into filters made of strong bagging. Even in this there are differences; and in 1880 I found at some even very large works long rows of bag-filters of the old shape, in which the oil slowly drains off. Much better is the following plan, often followed by English tar-distillers, the apparatus forming a rough kind of filter-press. A force-pump, or compressed air, forces the paste into a 4-inch main-pipe *a* (fig. 83), from which branch off a number of 1-inch T-pieces *b b*. Over their flanged ends sacks, *c c*, made of strong bagging, are tied with string. The sacks are open below, but are at first tied up there also. When filled they are about 1 foot in diameter and 4 or 5 feet long. They hang over a tank for receiving the oil draining off. When the forcing apparatus is set in motion, the sacks are filled with the anthracene-oil paste, of which the liquid portion at once begins to drain off. This goes on slowly, as the oils are viscid; but by increasing the pressure, until the gauge shows at last 1 atmosphere over-pressure,

Fig. 84.

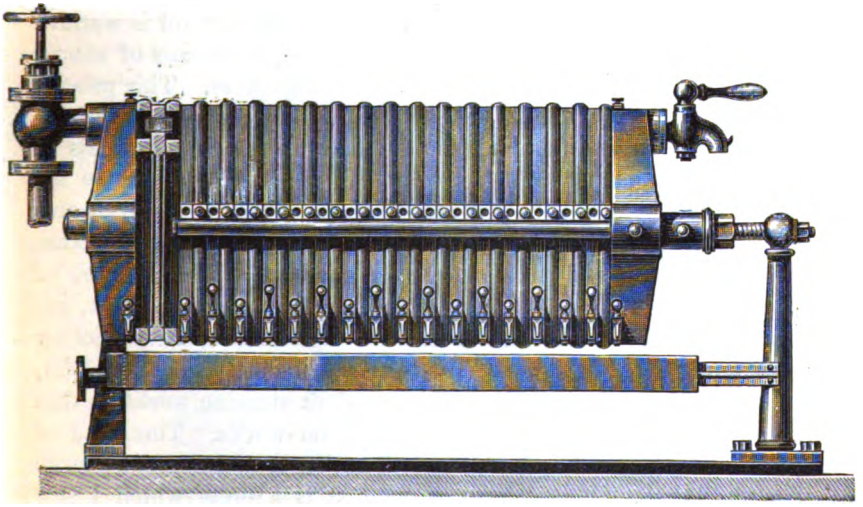


the draining is made much more speedy and complete, so that the contents of the sacks become nearly dry. Certainly some

considerable quantity of the finer crystals is forced through the bagging along with the oils; therefore the latter must be allowed to settle, and the deposit pressed again. When, in spite of pressure, nothing more runs out, the sacks are emptied. For this purpose a small carriage, *d*, is run on a line of rails underneath each sack in turn; the lower string is untied, and the falling-out of the contents assisted by knocking upon the sack. The rough anthracene thus obtained usually contains 12, or at most 15, per cent. anthracene by Luck's test.

Much more thorough and cleanly is the action of *filter-presses*,

Fig. 85.



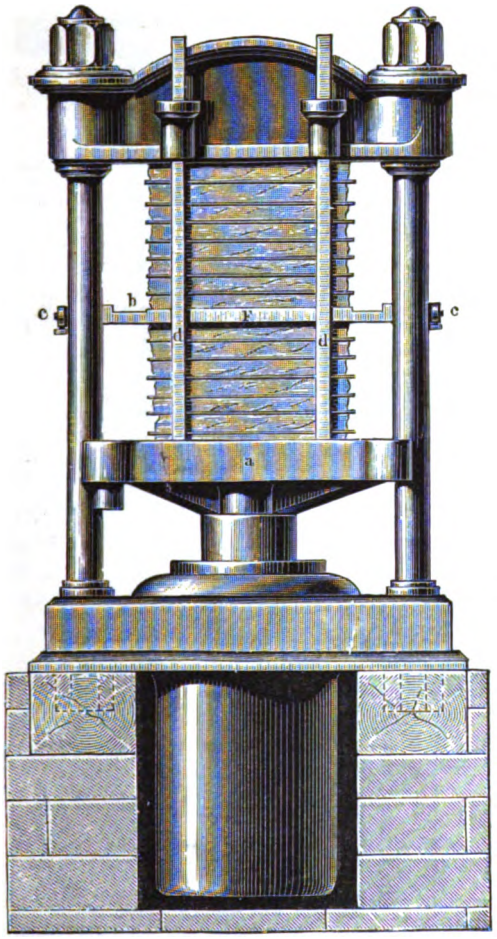
of which there is now quite a number of systems. That of Danek (manufactured by Dehne, at Halle) is represented in figs. 84 and 85. It seems unnecessary to give here details about the construction and treatment of filter-presses, always obtainable from the makers. The German works visited by me did not get more than 12 per cent. anthracene even with them; at a Dutch works 15 to 18 per cent. was obtained.

Centrifugal machines are also employed, and are said to answer, especially for thicker oils. At a German works it was asserted that 16 or 17 per cent. anthracene was obtained with these, which

is not easy to understand, since usually presses act better than centrifugal machines.

Now follows, in any case, pressing the product by *hydraulic presses*, either vertical or horizontal. Vertical presses (fig. 86) are most usual; they are just like those employed at beetroot-sugar works. The rough anthracene is put into cloths and so exposed to a gradually rising pressure, at last up to 300 atmospheres, till nothing more runs off. Sometimes, especially if the first draining has been effected in bag-filters only, the first pressing is done cold; and at one of the works visited by me they asserted getting up to 30 or 32 per cent. anthracene by mere cold-pressing. But mostly that strength is only attained by heating the oils, to make them more liquid and to melt the naphthalene. The application of heat takes place in various ways. Sometimes the oil is warmed before pressing, in a pan with double bottom, by means of steam, and is then pressed in an ordinary hydraulic press. This process will hardly yield such uniform results as real hot-pressing, especially in winter. In one factory, where the author saw this process at work, they came up to 35 per cent. In England the presses are surrounded by a wooden jacket, and steam is passed in during this operation. This process is not very cleanly; and the redistillation of the pressed oils is made more troublesome by the admixture of liquefied steam. Far the best, although more costly to erect, are presses like those used in the stearine-manufacture, whose hollow plates are *heated by steam*. The form shown here (fig. 87, p. 302), of the horizontal shape generally used at stearine works, is that employed at most German and Dutch tar-works. This kind of press is very efficient indeed, but it is rather troublesome to charge and discharge. Much more convenient is a press which I saw at a large English tar-works. It is a vertical press, each plate being hollow, and heated by a steam-pipe joined to it by a steam-tight socket, just like the plates in the horizontal presses. Each plate is at either side provided with a pin, sliding in slanting grooves worked in the sides of the perpendicular framework. On the rising of the ram the plates are all raised, and are ultimately subjected to as much pressure as is desired. But when the ram descends, each plate is stopped at a short distance from the next by the pins being caught and stopped, so that ultimately the plates appear fixed at equal intervals, leaving spaces between for introducing the cloths filled with crude anthracene.

Fig. 86.



In many cases presses with steam-heated plates must be decidedly superior to those with solid plates, heated merely by a wooden steam-jacket surrounding the whole press.

At most works the anthracene turned out by hot-pressing only comes up to about 30 to 33 per cent. in winter, and 33 to 36 per cent. in summer. At one German works I was, however, credibly informed that they got up to 50 or even 52 per cent., without any washing with naphtha, by three successive pressings,

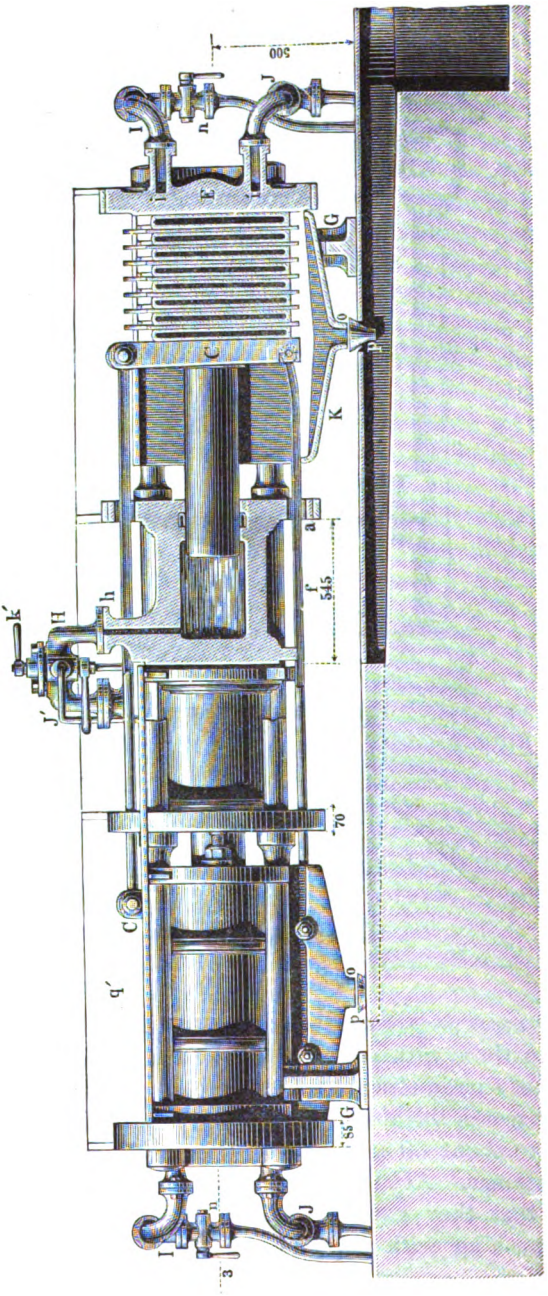


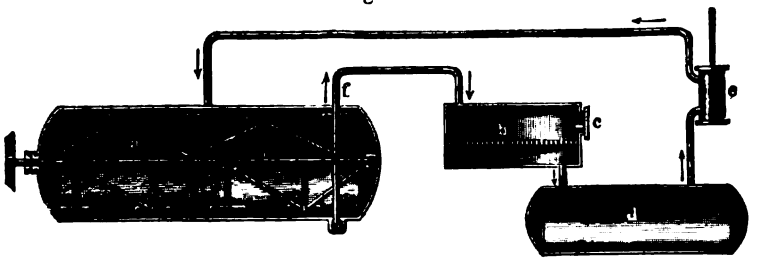
Fig. 87.

namely, 12 per cent. by the filter-press, 32 per cent. by the cold hydraulic press, and 50 to 52 per cent. by the horizontal steam-heated press.

Such work is, however, decidedly exceptional. The great majority of tar-works obtain such rich anthracene only by *washing*, *i. e.* treating with solvents of the impurities. As such, carbon bisulphide and alcohol have been thought of, but have hardly ever been employed, on account of their cost, their volatility, and the danger of fire. Very generally the "solvent naphtha" which is got on rectifying the light tar-oils, and essentially consists of xylenes, pseudocumene, and mesitylene, is employed. It distils between 120° and 190°, as we shall see in detail in Chapter XI. In this naphtha especially phenanthrene is much more soluble than anthracene. In England petroleum spirit of not more than 90° boiling-point is frequently used; that boiling at 100° dissolves too much anthracene. Creosote oil is also sometimes employed, as we shall see.

Before washing, the rough anthracene cake must be ground up into fine powder, which must also be done for sale. The grinding is effected by any sort of machine, such as horizontal mills, edge-runners, studded rollers, Carr's disintegrators, &c. The powder is usually stirred up with the naphtha in tight iron boilers, vertical or horizontal, fitted with a mechanical agitator and with a steam-jacket or an interior steam-coil. This is done for several hours,

Fig. 88.



gentle heat being applied; and the whole is then forced by compressed air into a filter, consisting of an iron box with an inner perforated false bottom, covered with canvas, where the solution is separated from the solid parts, the separation being much aided by the air-pressure. To avoid danger of fire, the filters, the tanks for receiving the oils, &c. must not communicate with the outer air. It would seem advisable to employ an arrangement sketched in

fig. 88 : *a* is the dissolving-boiler with its agitator; *b*, the filter, with the manhole *c* for removing the anthracene; *d*, the vessel for receiving the solution of the impurities in naphtha; *e*, an air-pump, aspirating the air from *d* and forcing it into *a*. Thus the whole of the paste is forced through the pipe *f* into the filter *b*, and the solution through it into *d*. In this way there is always the same quantity of air circulating, and a loss of naphtha is avoided as much as possible. Or else the mass may be treated in a centrifugal machine.

The *once-used naphtha* is always recovered, except the inevitable loss, by distilling the solution. The *residue* remaining in the still—consisting mainly of phenanthrene, along with some anthracene, methylanthracene, naphthalene, phenol, and unknown liquid lubricating-oils—is mostly not used for any thing except burning to make lampblack (p. 165), for which it is very suitable; but care must be taken that no water remains mixed with it. From this residue, as well as from other products of coal-tar distilling, *pure phenanthrene* might be produced in large quantities, if this substance ever became the starting-point for other useful products; at the present time it has practically no commercial value.

Some anthracene-refiners recover, by fractional crystallization, the anthracene, of which there is sometimes as much as 8 per cent. in these residues; but the majority seem to think this process too expensive, especially as this anthracene is always contaminated with methylanthracene.

The process carried out at one of the largest English tar-works is as follows :—The hot-pressed anthracene is ground up, and is well mixed in a closed machine with hot solvent naphtha, at a temperature of 77° C. The mixture is allowed to cool down to 21° C., and is now submitted to strong hydraulic pressing. In order to avoid escapes and danger of fire, the press is enclosed in a casing. The press-cakes are heated in a 3-ton still up to the melting-point of anthracene, the vapours being condensed in a small worm; and the melted anthracene is run out and solidified in iron boxes. The solution running out of the hydraulic presses is distilled in ordinary light-oil stills, and the distilled naphtha is used over again for washing anthracene. The residue remaining in the still is first treated for the extraction of some anthracene, by a process said to be quite a simple one, and is then either burned or worked into the creosote oil.

The washing with naphtha yields a product of at least 45 or 50, and with proper care upwards of 50 per cent.; the highest *reliable* amount given is 70 per cent., and refers to the above-mentioned article that had been previously brought to 50 per cent. by three pressings. At some English works, a few years ago, they proposed to get up to 85 per cent., but it is certain that this was never done on a commercial scale for any length of time (see below). On the other hand, some makers only get at most 30 or 40 per cent., by treating the rough anthracene, merely purified in the centrifugal machine or filter-press, with naphtha and then submitting it to hydraulic pressure. Hence the former process seems more rational than the latter.

At one of the largest English works they wash first with *crude* solvent naphtha (*i. e.* the second distillate of the light-oil still) as much as 56 or 60 per cent. is said to be obtained in this way.

Perkin* prefers washing with petroleum spirit, boiling between 70° and 100° C., which dissolves less anthracene than coal-tar oils, and yet removes the impurities sufficiently. Coal-naphtha sometimes dissolves 7 or 8 per cent. by weight of anthracene, which is difficult to recover. Carbazol is not removed by any solvent. The following table shows the solubilities of anthracene and some other bodies :—

	Petroleum spirit. B.p. 70–100°.	Benzol. B.p. 80–100°.	
Anthracene.....	0·115	0·967	per cent.
Phenanthrene.....	3·206	21·94	„
Carbazol.....	0·016	0·51	„
Dichloranthracene	0·137	0·62	„
Anthraquinone ...	0·013	0·166	„

Creosote oil is also employed for washing anthracene. Some believe that it is not a proper reagent for this purpose, as it dissolves more anthracene than phenanthrene &c.; but this must be erroneous, at all events with proper manipulation, since several tar-distillers employ creosote oil with great advantage, and some even believe this to be a valuable secret. In this way 40 per cent. anthracene can be obtained by the following process, which I have seen carried out with great success :—The first crude crystals, testing, say, 10 per cent. pure anthracene, after draining, are mixed with an excess of creosote oil at a temperature of 80°.

* Wagner's Jahresb. 1879, p. 1068.

The mixing being quite complete, the mass is allowed to cool down to 40°, and the crystals then obtained are subjected to hot pressure, when they will yield 40 per cent. anthracene, the creosote oil having dissolved far more of the impurities than of real anthracene. The tepid mother liquor is allowed to cool down to 25°, and thus a second crop of poorer anthracene crystals is obtained; and a third quality is got by allowing the second mother liquor to cool down to the ordinary temperature. The second product is put into the still, where the press-oil is distilled once more (see p. 309); the third product is treated along with fresh crude 10-per-cent. anthracene.

At another tar-works the process is as follows:—The rough anthracene is first passed through a filter-press, and then through an hydraulic press enclosed in a steam-casing. It is now washed with creosote oil in a steam-jacketed pan, with very well-designed horizontal agitating-gear, which thoroughly mixes up the warm liquid with the crystals. The mass is now filtered with the assistance of a vacuum, the same air circulating over and over again, as I had already proposed in 1880 (comp. p. 304, fig. 88). The anthracene thus gets up to 45 per cent.

It is especially contended that the washing with creosote oil removes that most disagreeable impurity in anthracene, viz. *paraffin*, which differs from ordinary paraffin by fusing at a much higher temperature, and is little soluble in either petroleum spirit or naphtha. But little of it suffices for disturbing the filtrations necessary in the subsequent operations; it resists pretty completely all the chemical processes to which anthracene and anthraquinone are subjected, and as it melts during the process of oxidizing the anthracene to anthraquinone, it is very troublesome. It has been stated * that the paraffins can be removed by dissolving the crude anthracene in a steam-jacketed vessel in 1·2 parts by weight of creosote oil distilling between 220° and 330°, and previously freed from phenols by washing with caustic soda. The solution is stirred till cold, the cooling being promoted by a stream of water, and the magma is pressed in a filter-press. The anthracene thus gets up from 28 to 36 or 40 per cent. by Luck's test; but it is often *not* quite free from paraffin.

Owing to the great danger of fire, the washing of anthracene and

* Fischer's (Wagner's) Jahresb. 1876, p. 466.

the recovery of the naphtha ought to be performed at some distance from the other erections, and not in very large apparatus.

The purification of anthracene by washing is frequently carried out, not at the tar-works, but by special anthracene-refiners or at the alizarin-works. The latter does not seem very rational—first, because this operation is much more in the style of tar-distilling than in that of colour-making, involving as it does the danger of contamination and of fire for those expensive products; secondly, because the tar-distiller can manufacture and recover the naphtha more cheaply than the colour-manufacturer.

A peculiar anthracene-purifying process was carried out for some time at Perkin's alizarin-works, and communicated under the seal of deep secrecy to one of the largest German works. The secret was even kept for years after the process had been proved to be unsuitable and had been given up. It is now known of what it consisted *. Anthracene is mixed with *caustic potash* and a little lime, and is distilled out of cast-iron gas-retorts, or wrought-iron retorts, 4 feet wide by 7 feet long, heated by flues below the bottom and along the side, and protected at the bottom against the direct action of the fire by fireclay slabs. These are connected by iron elbow-tubes with shallow iron boxes, in which the distilling anthracene condenses without further cooling. The covers of these boxes are put on loosely, so that the gases evolved at the same time can escape, and can even take fire without doing any harm. Caustic soda cannot be employed, because its fusing-point is too high; and as that of caustic potash is too low, quicklime is added. 200 kilog. of anthracene are ground up with 60 kilog. Montreal potash and 12 kilog. quicklime, during which operation the smell of ammonia is often perceived. The mixture is distilled at a low red heat. When this mass is diluted with water, a green solution is obtained which deposits greenish-blue flocks of extremely disagreeable smell. After the distillation the retort contains a porous, wax-like substance which takes fire on contact with air and deposits a sublimate of carbazol in the cooler parts. In fact this body was discovered by Graebe and Glaser on this occasion, and does not seem to be easily obtainable in any other way. The distillate from the retorts forms solid yellow pieces, containing about 40 per cent. real

* Auerbach, 'Das Anthracen,' 2nd ed. p. 11; Perkin, *loc. cit.*; Fischer's Jahresb. 1885, p. 467.

anthracene. From the residue in the retorts the caustic potash can be recovered by dilution with water and boiling with lime, or the residue is carbonized and used over again as crude potash; but unless a fine-dust chamber is interposed between the grate and the chimney, a great deal of potash is carried away by the draught as fine dust. The distillation with caustic potash is said to destroy the chrysene; but the destruction seems to extend to the anthracene, as shown by the following figures:—600 kilog. of 31-per-cent. anthracene cake were distilled with 180 kilog. caustic potash and 36 kilog. lime; the result was 380 kilog. 44-per-cent. anthracene, equal to a loss of 17½ kilog., or 10 per cent. When the considerable quantity of fuel for heating and the considerable wear and tear of the retorts are considered, it becomes apparent that this process is much too costly. But the anthracene purified in this manner is the best material for preparing chemically pure anthracene; comp. p. 129 (Auerbach, *loc. cit.*).

It is sometimes asserted that pitch-anthracene suffers a considerable loss in this operation, but tar-anthracene none at all (?).

Perkin (*loc. cit.*) states that in this process no more anthracene is lost than in distilling without potash, but 40 or 50 per cent. of the impurities are removed. The phenols, he states, are retained in the residue, also a non-volatile compound of carbazol, of which sometimes as much as 10 or 12 per cent. occurs in crude anthracene; so that the distillate consists essentially of anthracene and phenanthrene. The alkaline process is indispensable for the manufacture of alizarin by means of dichloranthracene; and all crude anthracenes, even the worst, yield the same good quality. Anthracene, washed before distillation with naphtha and petroleum spirit, yields again after distillation a considerable amount of impurities to those solvents (probably phenanthrene). If the process possessed all these advantages not counterbalanced by any drawbacks, it is difficult to understand why it has been given up again.

In 1884, at a large alizarin-works, I saw a process somewhat resembling that just described, viz. *fusing* (but not *distilling*) the anthracene, previously brought up to 50 per cent. by washing, with caustic potash (not to be replaced by caustic soda); the carbazol is thus removed as a potassium salt, and the anthracene comes up to 60 per cent.

By washing the anthracene distilled or fused with caustic potash, with solvent naphtha &c. in the manner described, p. 303, the

percentage of pure anthracene can be brought up to 70 per cent., or, as has been asserted, 80 or 90 per cent.; but the alizarin-makers do not seem to be inclined to pay the extra cost of such purification.

C. Caspers* proposes the following purifying process:—Well-pressed anthracene cake is mixed at from 12° to 15° C. with its own weight of paraffin oil, which dissolves naphthalene, phenol, cresol, &c. The residue is washed several times with paraffin oil (always at or below 15°), and last of all with methylated spirit, pressed, and dried at 100°. The product is said to contain 85 or 90 per cent. of anthracene fusing at 190°. This can be further purified by fusing and heating to 205°, when a dark green crystalline mass is formed, containing 95–97 per cent. anthracene, and yielding perfectly pure anthracene by sublimation (?). If the crude anthracene contains higher-fusing bodies, as pyrene, chrysene, &c., the washing with paraffin oil is carried on at such a temperature that the anthracene is dissolved, whilst chrysene &c. remain behind; on cooling the clear solution down to 15° the anthracene separates and is purified as above. (I am not aware that this process has anywhere been adopted.)

P. Currie† asserts that a larger yield of anthracene is obtained by adding sulphur to the tar-oils before distilling. A copious evolution of sulphuretted hydrogen takes place.

The *oils draining from rough anthracene* in the presses &c. are sometimes added to the creosote oil sent out for pickling wood; or else they are melted up with hard pitch in the stills in order to make soft pitch, refined tar, &c. (pp. 246 & 277); sometimes they are sold at a higher price as lubricators. It is most rational to distil them once more in ordinary tar-stills, to recover more anthracene, which no doubt previously existed in the oils, but has been kept dissolved by the liquid components, and hence can only be obtained (no doubt only partially) by a new fractionating; but some chemists hold that new anthracene is formed at the high temperature at which the distillation takes place. In other places the oils are only kept for several months, and the newly formed deposit is collected. E. F. R. Lucas‡ runs the tar-oil that distils between

* B. P. May 9, 1873; Chem. News, xxxix. p. 156.
† Chem. News, xxxi. p. 175.
‡ English patent, Jan. 24, 1874.

260° and 360° (undoubtedly after separating the anthracene) through red-hot tubes filled with bricks, and distils the dark oil formed thereby; the oil distilling at 360° is rough anthracene. Almost the same proposal has been patented once more by Hardman and Wischin (No. 4517, Nov. 7, 1878), who substitute coke for bricks. At the present time processes of this kind present very little hopes of financial success (comp. p. 90 *et seq.*).

A. M. Graham * describes the following process as the most suitable from practical experience on the large scale for extracting the anthracene from the filtered oils, which are frequently allowed to accumulate to an inconvenient degree, because the anthracene obtained from them is generally so impure as to be unsaleable. Fractional distillation, retaining only that portion of the distillate which comes over between 300° and 360°, is difficult and expensive. He prefers distilling, say, 1500 gallons of the filtered oils in a perfectly clean tar-still, free from tar and pitch, until crystals of anthracene begin to appear in the distillate on cooling. The distillation is then stopped; and after the temperature of the remainder has been sufficiently reduced it is run out into a tank and allowed to cool, when the anthracene crystallizes out in large quantity. A second and a third operation can be performed in this way; but usually it is found that the oil is sufficiently exhausted in one operation. The solid portion deposited in the tank will be found, after filtering and pressing, to contain at least 17 per cent. of real anthracene; and this can be easily raised to 36 per cent. by fractional distillation or by washing.

Watson Smith † was able to recover from the pressed oils, after treating them, hot, with a little concentrated sulphuric acid and caustic alkali, a large quantity of anthracene by repeated distillations. The last oil boiled at 260–290°; the fraction distilling between 260° and 280° remained quite colourless after long standing; it had a pleasant, hay-like smell, and the sp. gr. 1·04. It is miscible with paraffin oil and animal oils, and dissolves a considerable amount of tallow. It is also by itself a good lubricant. He could also isolate 0·28–0·45 per cent. crude anthracene cake from ordinary creosote oil, sold for pickling; even in the light oil, traces of anthracene were found.

* Chem. News, xxxiii. pp. 90, 168.

† Private communication.

H. Günther* employs the filtered oil for manufacturing black printer's ink. It is to be boiled with 10 per cent. of cupric chloride, which imparts a blackish-brown colour to it. The varnish is composed of 40 parts pitch or asphalt, 28 rectified oil of turpentine, 2 aniline violet, and 24 coal-tar oil.

Before anthracene, purified by any plan, can be converted into anthraquinone, it must undergo a suitable preparation (not merely by grinding) to reduce it to a sufficiently fine powder to facilitate the action of the oxidizing agents. For this purpose it is usually *sublimed* and precipitated in an extremely fine state of division by

Fig. 89.

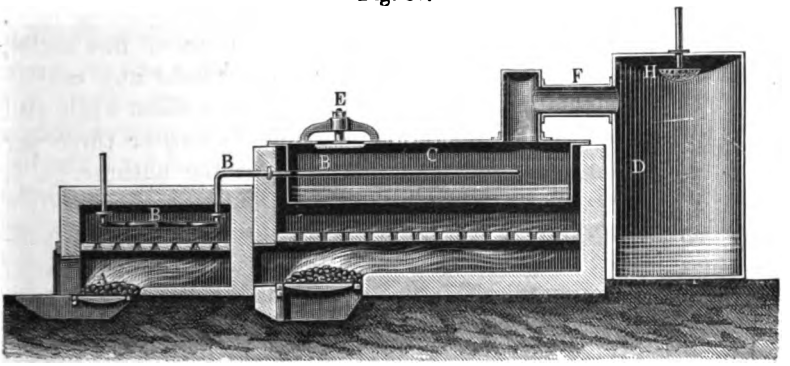
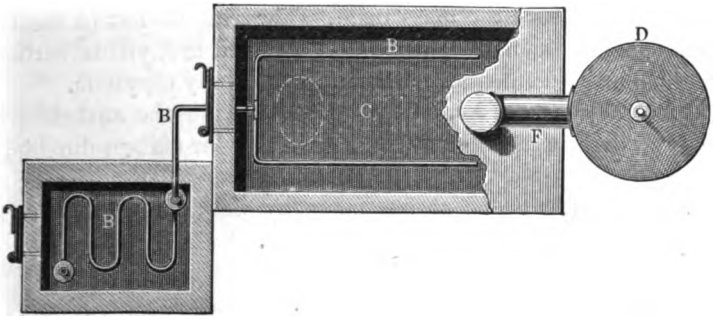


Fig. 90.



means of water. The sublimation is always effected by superheated steam, in an apparatus represented by figs. 89 and 90† (or in a

* German Patents No. 9566 (Oct. 28, 1879) and No. 11930 (May 8, 1880).

† From Wurtz, 'Dictionnaire de Chemie,' Supplément, p. 95.

deeper still, fitted up in a similar manner). The anthracene is placed in a shallow pan C, made of boiler-plate and heated from below, so that the anthracene fuses and forms a layer an inch or two in depth. The steam arriving in the pipe B is heated by the flame of the fireplace A to 220°–240°, and issues from the flattened tube B′ (which is perforated by many holes) to the melted anthracene, which it causes to sublime and carries away through the wide delivery-tube F into the brickwork or wooden chamber D. In this a jet of water, finely divided by the rose H, descends, condenses the steam, and suddenly precipitates the anthracene brought over in the state of finest division. The partial vacuum caused in this operation no doubt assists the sublimation in C. After draining, the anthracene, now a white mass of fine scales, can, after passing it through a sieve to separate any coarser particles carried along in the melted state, be oxidized while still wet. The loss in this operation amounts to two or three per cent. According to Wurtz the strength of the anthracene is thereby raised from 50 to 60–65 per cent.; but this is evidently a mistake. According to Auerbach (*l. c.* p. 11) the effect of the sublimation is not a purification at all, but only a mechanical division. At any rate the purification cannot exceed the loss, above mentioned, of two or three per cent.; and this has been confirmed by all the alizarin makers whom I have consulted. Sometimes no fire is applied to the still from without; but then the steam must be superheated to at least 300°, and must be blown into the mass itself. The residue left in the still, when being cautiously distilled over a naked fire, yields carbazol, phenylnaphthyl carbazol, pyrene, and especially chrysene.

E. Perret (Wurtz, *loc. cit.*) proposes heating the anthracene to 250° and driving the vapour, mixed with air or carbon dioxide, by means of a fan-blast into chambers to be condensed in the dry way. A similar proposal was made by Schuller*; it does not seem so rational as the wet condensation.

Statistics.

The yield of anthracene varies both with the quality of the tar and with the care bestowed upon extracting it. While Scotch tar yields little or no anthracene, the German and Dutch works obtain

* Ber. deutsch. ch. Ges. 1870, p. 548.

from 0·3 to 0·35, at most 0·45, parts of pure anthracene (Luck's test) from 100 parts by weight of tar. In England the yield is much more considerable: North-Country tar, on the average, yields 0·5; London tar from 0·8 to 0·9 per cent. by weight of pure anthracene. From a communication by Mr. J. Leahy, Thurston Chemical Works, Sittingbourne, it appears that at that works the average yield of anthracene over 18 months has been equal to 0·676 per cent. pure anthracene on the coal-tar distilled.

H. Elliott* states the yield of anthracene from water-gas tar as 2·63 per cent.

Compare also the statements in Chapter V. p. 260 *et seq.*

W. H. Perkin† estimates the yearly production of anthracene in the United Kingdom at about 6000 tons 30 per cent., or nearly 2000 tons pure anthracene. This is largely in excess of the present requirements of the manufacture of alizarin. This seems to make it a hopeless undertaking to manufacture anthracene by distilling pitch (comp. p. 284), or by superheating petroleum residues and the like (pp. 90 & 309), or by distilling rosin with alkali, as patented by R. Irvine (B. P. 4276, 1882).

The principal consumption of anthracene takes place in the German alizarin-works, which, according to reliable statistics, in 1880 worked up 1400 tons of *pure* anthracene, 200 tons of which were supplied by German tar-distillers, the remainder principally by English distillers.

The fluctuations in the price of anthracene are enormous. Perkin (*loc. cit.*) paid per lb. in 1870–1871 1*s.* 6*d.*, in 1872 1*s.* 6*d.* to 5*s.* and even 5*s.* 6*d.* The value in 1881 was about 3*s.*, in 1886 about 9*d.*

Properties and Analysis of Anthracene.

The properties of *pure* anthracene have been described, p. 128 *et seq.*

Rough anthracene, before sublimation, is a brownish-green friable mass, still containing most of the substances mentioned on p. 296.

* Amer. Chem. Journ. vi. p. 248 (1884).

† Journ. Soc. Chem. Ind. 1885, p. 433.

Zeidler* has made an extensive investigation of crude anthracene and has found the following substances:—

I. Insoluble in acetic ether: anthracene, chrysene, and other bodies not yet examined.

II. Soluble in acetic ether.

A. Soluble in cold 40-per-cent. alcohol.

1. Insoluble in carbon disulphide: carbazol.
2. Soluble in carbon disulphide: phenanthrene, fluorene, hydrocarbons melting at 92°·5.

B. Soluble in moderately warm benzene: synanthrene, hydrocarbons melting at 97° and 104°.

C. Soluble in hot benzene: anthracene, pseudophenanthrene.

D. Insoluble in hot benzene: carbazol.

Methyl-anthracene is not mentioned here, although it occurs largely in some descriptions of crude anthracene.

It is not a very easy task to distinguish the different substances occurring in crude anthracene, and we cannot here go into this matter, which does not interest the tar-distiller so much as the alizarin-maker and the scientific chemist. We will only mention that the identification of the different hydrocarbons is often promoted by the characteristic combinations they form with picric acid. Watson Smith† has proposed to employ the fused chlorides of antimony and bismuth for descriminating the solid hydrocarbons.

Looking at the high value of anthracene, and the extremely varying percentage of pure anthracene in the rough product, it is evidently of the greatest importance to possess a reliable method of analysis. Formerly this was merely attempted by the action of solvents for the impurities, which, however, is so imperfect that those methods have been almost entirely replaced by Luck's method, which certainly requires some manipulative skill. But as the old methods are not yet altogether obsolete, we must here describe them.

Each of them was intended to remove the foreign matters and to leave pure anthracene behind. Evidently this cannot be done with any approach to exactness; for, on the one hand, the impurities are not entirely soluble (some are even less so than anthracene

* Ann. Chem. Pharm. vol. cxci. p. 285.

† Chem. News, xl. p. 26.

itself) in the liquids employed; on the other hand, the latter dissolve sensible quantities of anthracene as well. Hence different solvents yield quite discordant results; but, apart from the evident impossibility of thus ascertaining the true percentage of pure anthracene, each method by itself gives pretty constant results, on the condition of strictly keeping to the same mode of manipulation, which must be agreed upon between buyer and seller. In the sale-note the solvent employed must be specified (*e. g.* whether carbon bisulphide or alcohol), its quantity, its specific gravity in the case of alcohol, and the exact way of manipulating it stated. Thus, if the product be of an oily nature, a higher value will be found if the sample be pressed before analyzing it, because the oils left in augment the solvent power of the liquid employed for anthracene itself.

The following are the methods employed in practice:—

1. *Alcohol Test* (*Spirit Test*).—Triturate the sample well in a mortar; weigh out 20 grams, which stir well up in a beaker with 150 grams of alcohol of the strength stipulated in the sale-note (usually sp. gr. 0·825); cover the beaker with a watch-glass, gradually heat to boiling, and then cool by placing it in water of 15°·5. After an hour the liquid is decanted through a filter, and the undissolved part is gradually washed with alcohol of the same strength as before, and at the temperature of 15°·5, till the filtrate and washings together amount to 400 cub. centim. If there is sand clearly perceptible at the bottom of the beaker, it is kept back; the remainder is placed in a weighing-glass, dried at 100° in a water-bath, and weighed. Its weight multiplied by 5 is accepted as the percentage of anthracene.

According to Auerbach (*loc. cit.*) 20 grams of anthracene cake are heated with 100 cub. centim. of alcohol of 98 per cent., and the washing continued to a bulk of 300 cub. centim.

In order to test the so-called pure anthracene of this operation for foreign insoluble bodies, sometimes 5 grams are boiled with as much alcohol as suffices to dissolve all the anthracene, and the liquid is filtered while hot. The residue is washed with boiling alcohol; and the residue insoluble in this liquid is deducted from the percentage found above; if its weight amounts to more than 1 per cent., it must be considered an adulteration.

In any case the melting-point of the so-called anthracene is determined. It is put into a finely drawn-out glass tube, in which

it is to occupy a space of about an inch in length; the tube is fastened by means of a small piece of elastic tubing to a good thermometer; and both are immersed in a paraffin bath, which is slowly heated. The point at which the first drop runs down is taken as the melting-point. After the mass has completely liquefied, the lamp is removed and the temperature at which solidification again takes place is observed. The mean between this and the point found above is the *mean melting-point*; it ought not to be below 190°.

Sometimes the following course is taken:—190° (or some other temperature) is accepted as the standard melting-point; and it is ascertained how much substance having this melting-point is obtained by employing an indefinite quantity of alcohol, but always of the same specific gravity (say 0·825). A sample is treated as above, and the melting-point ascertained. If this be 190°, nothing further is requisite; but if above that, a new test is made with less alcohol; if below, with more alcohol. If, say, sample No. 1 has been boiled with 150 cub. centim. alcohol and washed to 400 cub. centim., and has then yielded 40 per cent. melting at 195°, sample No. 2 is boiled with only 100 cub. centim. alcohol and washed to 300 cub. centim.; this yields more, say 49 per cent., melting at 188°. The quantity melting at 190° is then found by the proportion:—

$$195-188 : 49-40 = 195-190 : x,$$

where x is the amount to be added to the lower percentage. On carrying out the calculation we get

$$x = \frac{9 \times 5}{7} = 6{\cdot}4;$$

hence the sample contains $40+6{\cdot}4=46{\cdot}4$ substance melting at 190°.

The spirit test is wrong in principle; for alcohol dissolves some anthracene and does not remove the chrysene. These two opposite errors may compensate each other by accident, but certainly not in most cases; and this method is therefore undoubtedly an inaccurate one.

2. *Bisulphide-of-Carbon Test.*—10 grams of the well-mixed sample are shaken in a stoppered bottle with 30 cub. centim. carbon bisulphide, and allowed to stand an hour at 15°·5. The undissolved matter is thrown on a filter, the bottle is washed out

with 30 cub. centim. of carbon bisulphide; but any sand is left behind. After the liquid has run through, the filter is pressed gently, but quickly, first with the fingers and then between blotting-paper in a strong press. The insoluble matter is put on a watch-glass, dried for an hour at 100°, and weighed; its weight, multiplied by 10, indicates the percentage. The "mean" melting-point of the substance ought not to exceed 212–214°.

Déhaynin heats 20 grams of anthracene with 40 cub. centim. of carbon bisulphide for 20 minutes, with constant stirring, cools down to 15°, filters through a tared filter, and washes with so much carbon bisulphide that the total amounts to 100 cub. centim. The residue is dried, weighed, and taken as pure anthracene.

Perkin grinds up 50 grams of anthracene with 10 fluid-ounces of petroleum spirit of sp. gr. 0·740, passes through canvas, and washes the vessel and the residue with another 20 fluid-ounces. The filter is squeezed out, first by hand, then in a vice. The residue is powdered, put into a bottle holding 6 or 7 ounces, and strongly shaken up for 2 or 3 minutes with 5 ounces of carbon bisulphide. It is then put upon a tared filter, pressed between blotting-paper, dried, and weighed. The product ought to show a mean melting-point of not below 200°, nor above 212°.

The bisulphide-of-carbon test, or the same combined with the application of petroleum spirit, has kept in use for a long time, although it is perhaps even worse than the spirit test. Chrysene is very little soluble in carbon bisulphide; hence by this process a product may be obtained which shows the proper melting-point and yet is not anthracene. Besides, carbon bisulphide dissolves 2 per cent. of anthracene; and, owing to its quick evaporation, very discordant results will be obtained by different chemists, according to the difference of manipulation, the deviations extending to 4 or even to 6 per cent.; 2 or 3 per cent. is quite usual here, as well as with the spirit test.

A comparison between the results of the spirit and bisulphide-of-carbon tests shows that the two do not bear a constant proportion to each other. In the case of low products the alcohol test indicates four times as much as the carbon-bisulphide test; with higher percentages the discrepancy becomes less and less, the alcohol test uniformly giving a much higher result; only at the highest percentages does the inverse ratio take place. There are also considerable differences between the melting-points. This is

proved by a table given by Versmann as the result of 30 duplicate tests according to both methods, which need not be repeated here.

3. *Anthraquinone Test.*—Anthraquinone, the product of the oxidation of anthracene, obtained in the manufacture of alizarin, appears in the pure state as a mass of pale yellow needles, when precipitated from solutions, but in the shape of long, thin, golden-yellow needles when sublimed. It fuses at 277° and boils a good deal above the boiling-point of mercury, but it sublimes very much below that. It is insoluble in dilute acids or alkalies, and is not even affected by hot concentrated hydrochloric acid or solution of caustic alkalis, but it dissolves unchanged in concentrated sulphuric acid at 100°, and is again separated by dilution. It is very little soluble in alcohol and ether, but more so in hot benzene.

It had been previously recognized that the oxidation of crude anthracene to anthraquinone, and the estimation of the latter, is the only reliable method of analysis in this case. But the merit of investigating all the points necessary to elaborate a system of testing belongs to E. Luck, whose name is justly attached to this test. Luck had first to ascertain whether a weighed quantity of rough anthracene, on oxidation with glacial acetic acid and chromic acid, yields the theoretic quantity of anthraquinone, whether the latter is not oxidized further by long contact with chromic acid, and what is the behaviour of the regular (accidental or purposely added) accompaniments of anthracene during the chromic-acid treatment. Luck's results were as follows:—

I. Pure anthracene, dissolved in glacial acetic acid and treated at boiling-heat with 3–4 parts of chromic acid, yields 99·4 per cent. of the theoretically calculated quantity of anthraquinone.

II. Pure anthraquinone, dissolved as above and boiled with 3–4 parts of chromic acid for 2 hours, on dilution with water yielded the original quantity of the anthraquinone employed (employed 0·447, recovered 0·446 gram).—But more recent experiments refute this statement; by successive treatment of anthraquinone with constantly renewed quantities of glacial acetic acid and chromic acid 1 gram of 93·2 per-cent. anthraquinone was reduced to 0·576 gram. Hence anthraquinone does not resist the oxidizing action of chromic acid to the extent assumed by Luck.

III. The substances accompanying or contaminating anthraquinone are, by a sufficiently prolonged chromic-acid treatment, completely converted into bodies soluble in acids or alkalis, and

can thus be separated from it. This holds good of phenanthrene, chrysene, paraffin, bitumen, &c.

Luck's method in its original shape was as follows :—

1 gram of the rough anthracene is dissolved in a small flask in 45 cub. centim. of boiling glacial acetic acid. If required, the solution is filtered quite hot through a small filter, and a solution of 10 grams chromic acid in 5 cub. centim. of water and 5 cub. centim. of glacial acetic acid is added in small quantities, so that the liquid remains constantly boiling. The chromic-acid solution is run in till a distinct and remaining greenish-yellow colour appears, or till after prolonged boiling a drop of the solution, put on a bright silver coin, produces after a few minutes a reddish spot of silver chromate. The liquid is now allowed to cool, is gradually diluted with 150 cub. centim. of water, filtered after a few hours; the anthraquinone remaining on the filter is washed, first with water, then with hot, very dilute solution of caustic potash, then again with water, and dried at 100°. After weighing, the anthraquinone is quickly removed from the filter, the latter is weighed, and its weight is deducted from the original gross weight. To the net weight thus obtained an addition of 0·01 gram is made, because, if according to the above prescription 50 cub. centim. of glacial acetic acid and 150 cub. centim. of water have been employed, 10 milligrams remained dissolved in the filtrate.—Commercial chromic acid often contains lead; in this case the anthraquinone, after washing with water and alkali, must be treated with a hot solution of ammonium acetate.

It was soon found that even in this way no perfectly accurate results were obtained. A portion of the impurities is not completely oxidized, and is thus estimated as anthraquinone. Hence Luck subsequently prescribed treating the latter with an alkaline solution of potassium permanganate. The anthraquinone, after washing with alkali, is washed into a small beaker or dish, is rendered faintly alkaline, heated to boiling, and a solution of potassium permanganate is gradually added, till it is no more reduced and the green colour is changed into pale pink. Now a little oxalic acid and sulphuric acid are added, to reduce the excess of potassium permanganate, and to dissolve the manganese dioxide formed. The whole is now filtered. Upon the same filter the precipitate is washed to perfect neutrality, then with dilute solution of sodium carbonate, then again with water, dried at 100°,

and weighed. Luck states that usually 10 grams of chromic acid are quite sufficient, but exceptionally 15 grams may be required for perfect oxidation. Auerbach (*loc. cit.*) states that this indefiniteness sometimes produces awkward results. Thus a sample of rough anthracene, in four tests with 10 grams of chromic acid, always yielded 26 per cent., but in six tests, with 15 grams of chromic acid, only 23 per cent., although in both cases an excess of chromic acid was present. Probably a small excess of chromic acid in the presence of chromium acetate does not oxidize anthracene any further; this requires a larger excess. It would therefore be best to prescribe in all anthracene-contracts 15 grams of chromic acid for 1 gram of rough anthracene, which seems to be sufficient in every case. The time allowed for the oxidation has no influence; three or four hours suffice, and six or eight hours do not alter the result.

An objection to Luck's method is the hot filtration which is prescribed as sometimes neccssary. Organic bodies are anyhow destroyed during the oxidation; inorganic ones, which are mostly non-volatile, as sand, are best estimated by igniting a sample of crude anthracene. But if the substances insoluble in glacial acetic acid are to be estimated, it is in any case much safer to extract a weighed sample of crude anthracene completely, than to filter the mixture intended for analysis whilst hot, in which operation a portion of the anthracene is lost by evaporation of the acetic acid and crystallization on the filter.

J. T. Brown* proposes making the analyses more correct by taking a larger average sample, and by other precautions. He weighs off 50 grams of crude anthracene, and at the same time measures off 250 cub. centim. of petroleum spirit. With a portion of the latter he triturates the anthracene in a mortar so as to form a thin cream, pours it into a weighed filter (taking care to leave in the mortar any grit or sand that may be present), and employs the rest of the petroleum spirit in rinsing out the mortar and washing the precipitate on the filter. After draining, fold carefully, press between blotting-paper, dry at from 60° to 80°, and weigh. Crush the contents of the filter to fine powder, and weigh out the gram required for the anthraquinone test.—This proposal is useless; for the temperature, the specific gravity of the petroleum spirit, &c. will essentially influence the result.

* Chem. News, xxxiv. p. 136.

It is a further objection to Luck's method that even after treating with permanganate the anthraquinone is not yet pure. In this case it would dissolve without change in sulphuric acid, and would only at a temperature above 200° be converted into a sulphonic acid. But Luck's quinone when treated with concentrated sulphuric acid turns blue or brown, which proves the presence of foreign bodies; even if the acid remains colourless, a coloured solution is obtained by subsequently boiling the quinone with dilute solution of caustic soda. Hence the results of purifying by permanganate vary from those of the purification with sulphuric acid (to be described anon) to the extent of from 1 to 8 per cent.

For this reason Meister, Lucius, and Brüning* have proposed the following method of analysis, which is now well-nigh universally adopted, and is sometimes designated as the "Höchst test." Take 1 gram of anthracene, put it into a flask with condenser of 500 c. c. capacity, add to it 45 c. c. of glacial acetic acid, and heat to ebullition. To this solution, which is kept boiling, add drop by drop a solution of 15 grams of chromic acid in 10 c. c. of glacial acetic acid and 10 c. c. of water. The addition of the chromic solution should occupy two hours, after which the liquid is kept boiling for two hours longer. The flask with its contents is to stand twelve hours, then to be mixed with 400 c. c. of cold water, and again kept standing for another three hours. The precipitated anthraquinone is now collected on a filter and washed, first with pure water, then with boiling dilute alkaline solution, and finally with pure water hot. The quinone is now washed from the filter into a dish and dried at 100° C.; it is then mixed in the same dish with ten times its weight of fuming sulphuric acid of 68° Baumé (sp. gr. 1·88) and heated to 100° C. for ten minutes on a water-bath. The quinone solution thus obtained is poured into a flat dish and kept for twelve hours in a damp place to absorb water; then add 200 c. c. of cold water to the contents of the dish, collect the precipitated quinone on a filter, and wash first with pure water, then with boiling alkaline solution, and finally with pure water hot. The anthraquinone is now placed in a dish, dried at 100°, and weighed. After volatilizing the quinone by heating the dish, the latter is weighed with the particles of coal and the ash. The difference between the two weights gives the weight of the anthraquinone obtained; and it is to be

* Zeitschr. für analyt. Chemie, xvi. p. 61.

calculated in the usual manner into anthracene (multiplication by coefficient 0·8558). A correction for the quinone dissolved in the acetic acid is, under the conditions here prescribed, not necessary or admissible.

The following Table will save a calculation :—

Quinone.	Anthracene.	Quinone.	Anthracene.	Quinone.	Anthracene.	Quinone.	Anthracene.
1	0·86	26	22·26	51	43·65	76	65·05
2	1·71	27	23·11	52	44·50	77	65·90
3	2·56	28	23·98	53	45·35	78	66·77
4	3·42	29	24·83	54	46·21	79	67·62
5	4·28	30	25·67	55	47·07	80	68·46
6	5·14	31	26·53	56	47·93	81	69·32
7	5·99	32	27·38	57	48·78	82	70·17
8	6·86	33	28·23	58	49·65	83	71·02
9	7·71	34	29·09	59	50·50	84	71·88
10	8·56	35	29·95	60	51·35	85	72·74
11	9·42	36	30·81	61	52·21	86	73·60
12	10·27	37	31·66	62	53·06	87	74·45
13	11·16	38	32·53	63	53·91	88	75·32
14	11·98	39	33·38	64	54·77	89	76·17
15	12·84	40	34·23	65	55·63	90	77·02
16	13·70	41	35·09	66	56·49	91	77·88
17	14·55	42	35·94	67	57·34	92	78·73
18	15·42	43	36·79	68	58·21	93	79·58
19	16·27	44	37·65	69	59·06	94	80·44
20	17·12	45	38·51	70	59·91	95	81·30
21	17·98	46	39·37	71	60·77	96	82·16
22	18·83	47	40·22	72	61·62	97	83·01
23	19·68	48	41·09	73	62·47	98	83·87
24	20·54	49	41·94	74	63·33	99	84·73
25	21·40	50	42·79	75	64·19	100	85·58

According to the investigations of F. H. Davis and Lucas*, the result of Luck's test does not at all agree with that of the carbon-bisulphide test; the latter mostly shows a great deal too much. But in one case Davis obtained from the same sample by the alcohol test (sp. gr. 0·825) 34·645 per cent., melting-point 187°·5; by carbon bisulphide 23·250, melting-point 198°·2; by Luck's test, 28·358. Lucas found by the carbon-bisulphide test in three cases 0·4–2·7 per cent. too little, in seventeen cases 2·5–23·78 per cent. too much. He confirmed Luck's opinion that all the substances accompanying anthracene are by the chromic-acid treatment converted into bodies soluble in dilute alkali.

G. Schultz† holds that in one respect Luck's test gives too un-

* Chem. News, xxix. p. 169, xxx. p. 190, xxxi. p. 209.

† Ber. deutsch. chem. Ges. 1877, p. 1051.

favourable a result, since chromic acid converts methylanthracene into soluble anthraquinone-carbonic acid and thus removes it, whilst in actual manufacturing methylanthracene is converted into a quinone, and this into methylalizarin, which has as much tinctorial power as alizarin. This is, however, not so; the products formed from methylanthracene impart to the alizarin colours a very obnoxious shade, and hence alizarin-makers dread methylanthracene almost as much as paraffin (comp. Römer and Link, Ber. deutsch. chem. Ges. 1883, p. 695). It occurs, however, in large quantities only in the alizarin recovered from the washing naphtha (p. 304).

Holland* objects to Meister, Lucius, and Brüning's prescription (the "Höchst test"):—1st, that the 55 c. c. of glacial acetic acid, diluted though it be with 400 c. c. of water, still retains anthraquinone in solution, viz. on an average 0·0023 gram; 2nd, that boiling water dissolves some quinone, viz. 500 c. c. water, 0·0019 quinone; 3rd, that in thrice washing the quinone from the filter a small loss is inevitable, which he estimates at 0·0020 gram; even with the most careful manipulation the total loss amounts to 0·0065 quinone = 0·0055 anthracene, and this quantity ought always to be added to that found. (According to information received by me from the most competent quarter, Holland's corrections are inadmissible, as the anthraquinone obtained by the "Höchst test" is itself not quite pure, but contains methylanthraquinone, anthraquinone-carbonic acid, and paraffin, which may cause an error of 1 per cent. and upwards in the opposite direction to Holland's corrections.)

Schwarz† believes the best test for crude anthracene to consist in washing it with a cold saturated solution of anthracene in glacial acetic acid. This test is not in use anywhere.

Anthraquinone, as obtained by the Höchst test, ought to be crystallized and of pale yellow colour. An orange or red colour would show the presence of other quinones, especially phenanthrene and chrysenequinone. The latter is also recognized by the production of an indigo-blue coloration on adding the sulphuric acid. With impure anthraquinone both the acid filtrate and the alkaline washings are deeply coloured. The above-mentioned quinones do not prevent the crystallization of anthraquinone, but

* Printed circular, dated Manchester, Feb. 1879.

† Wagner's Jahresb. 1877, p. 921.

this is done by the quinone, $C_{16}H_9NO_2$, produced by the oxidation of the imido-phenylnaphthyl (see below), which is one of the sources of the so-called "amorphous particles." This impurity can be destroyed by a somewhat longer-continued heating with sulphuric acid, which ought hence never to be omitted when crude anthraquinones of unhealthy appearance have been obtained (Allen, Commercial Organic Analysis, 2nd ed. ii. p. 532).

Paraffin (the objectionable presence of which in some samples of anthracene has been mentioned on p. 306) can be detected and determined in the following manner:—10 grams of the sample is heated with 200 grams of strong sulphuric acid in a water-bath for about ten minutes, or until the anthracene is completely dissolved. Any considerable quantity of paraffin will rise to the surface in the form of oily globules. The solution obained is cautiously poured into 500 c. c. of water contained in a tall beaker. After being thoroughly stirred the liquid is allowed to cool, when any paraffin will rise to the surface, and having solidified, can be removed, washed with a little cold water, dried between blotting-paper and weighed. From 2 to 5 per cent. is the quantity commonly present in Scotch anthracenes (Allen, 'Commercial Organic Analysis,' 2nd ed. ii. p. 529).

Imido-phenylnaphthyl, which impedes the purification of the anthraquinone, can, according to B. Nickels*, be discovered by dissolving the sample of crude anthracene in hot benzene, filtering through a dry filter, and examining the solution with a spectroscope. The above substance produces a highly characteristic absorption-spectrum, showing two broad and well-defined black bands between the F and G lines and another, slightly more refrangible than G.

It should be stated that the anthraquinone test, even in its most perfected form, does not give absolutely reliable results. Sometimes a certain description of quinone, which is as beautifully crystallized as possible, and cannot be distinguished by any outward marks, yields very inferior alizarin. The cause of this is as yet unknown; but it is most likely that the quinone in such cases contains not merely pure anthraquinone but also the derivatives of hydrocarbons other than anthracene, which are so similar to anthraquinone in appearance and chemical properties, that so far no means are known of separating them from anthraquinone

* Chem. News, xl. p. 270, xli. pp. 52, 95, 117.

itself. Some have asserted that these inferior quinones are more easily soluble in glacial acetic acid; but no proof of this has been given, and we must hold this question as not yet solved.

Mr. B. Nickels has communicated to Mr. Allen the following process for testing anthracene, employed at some alizarin-works, of which the aim is to work as closely as possible by the method of oxidation pursued on a manufacturing scale.

With this view, the oxidation is carried out in very dilute liquids, under which conditions the anthracene is converted into anthraquinone, while the foreign hydrocarbons suffer but little change. On subsequently treating the product with sulphuric acid, the unoxidized hydrocarbons are converted into soluble substances, and a nearly pure anthraquinone results, which may be obtained perfectly pure by a second treatment with acid. In experienced hands and with careful manipulation this miniature factory-operation gives constant and very accurate results.

The chief source of error is incomplete conversion of the anthracene itself, and its consequent solution and loss on treating the crude anthraquinone with sulphuric acid; but this can be guarded against by a microscopic examination of the oxidation-product. The following are the details of the process:—10 grams of the sample of anthracene are ground to an impalpable powder in a mortar; 20 grams of potassium bichromate are added, and the whole thoroughly mixed by grinding. The mixture is transferred to a large porcelain dish, 1 litre of water added, and the liquid brought to boil. 30 grams of sulphuric acid are diluted with about an equal measure of water, and added in successive small portions during about one hour, the liquid being kept constantly boiling and frequently stirred. The boiling is continued for three hours after the whole of the acid has been added, care being taken to replace the loss by evaporation by adding boiling water, as it is only in such dilute solution that the anthracene can be converted into anthraquinone, without simultaneously oxidizing the accompanying substances. The liquid is next filtered, and the filter washed with hot water till all traces of chromium-salts have been removed. The contents of the filter are then dried at 100° and weighed. The weight obtained represents the yield of "crude factory anthraquinone," and may contain from 40 to 50 per cent. of the pure substance. Before purifying this crude product a minute quantity of it should be dissolved in hot benzene, and a drop of

the solution placed on a glass slide. After allowing the dissolved matters to crystallize, a glass cover is applied, and the slide observed under the microscope. Unoxidized anthracene, if present, assumes the form of sharp, tabular, overlaying plates; while the anthraquinone will be in the form of distinct needles and stellated groups. Naphthalene is the only associated hydrocarbon which at all simulates anthracene, but with a little care it is readily distinguished. The other bodies liable to be present assume more or less characteristic forms, which cannot be confounded with anthracene. Examined with the polariscope, the appearances of anthracene and anthraquinone are extremely characteristic. If no unoxidized anthracene be detected under the microscope, the purification of the crude anthraquinone is proceeded with as follows:—

The crude anthraquinone is next treated in a small shallow dish with four times its weight of strong sulphuric acid; and the mixture is heated in the water-oven for about one hour and a half, being frequently stirred during that time. The capsule is then placed in a box, or under a bell-jar, side by side with a larger dish of boiling water, so as to maintain a damp atmosphere, which causes the gradual dilution of the acid and facilitates the crystallization of the anthraquinone. After twelve hours the capsule is removed and immersed in about 500 c. c. of water, which is then boiled. After cooling, the liquid is filtered, the residue washed till free from acid, and then treated on the filter with a dilute boiling solution of caustic soda (sp. gr. 1·04), till the filtrate runs through colourless. The alkali is then washed out with warm water, and the substance on the filter dried at 100° C. and weighed. The product has a greenish-grey or slate-grey colour, is highly crystalline, and contains from 80 to 95 per cent. of real anthraquinone. A known weight of it (about 1 gram) is further purified by heating it in the water-oven for ten minutes with ten times its weight of strong sulphuric acid. The product is exposed to a damp atmosphere, dissolved in water, filtered, treated with alkali, &c., and weighed in a manner exactly similar to that previously adopted. The usual precautions respecting the treatment of the anthraquinone on the filter should be observed here. The weight of pure anthraquinone obtained is calculated first on the grey product, and this on the original sample, or intermediately on the crude anthraquinone, if some of the latter was not recovered

from the benzene solution used for its microscopic examination. The pure anthraquinone found, multiplied by ·856, gives the real anthracene in the sample.

Lastly, we shall mention a plan for *estimating the quantity of anthracene in tar*, although it does not appear to be very correct, the quantity of tar worked upon being so very small. C. Nicol* distils 20 grams of tar, and collects the vapours in a U-tube kept at 200° C. by means of a paraffin-bath. Here the more volatile oils go away, whilst anthracene &c. remain behind. Since a little remains in the neck of the retort, this is cut off, the glass is pounded and added to the distillate in the receiver. This is now dissolved in glacial acetic acid, and the anthracene estimated by Luck's test. (In testing tar, I distil at least one litre at a time, and estimate the anthracene in the oil coming over between 270° and the end of the distillation.)

* Zeitsch. f. analyt. Chemie, 1876, p. 318.

CHAPTER VIII.

CREOSOTE OIL.

In this Chapter we treat of the employment or further refining of those distillates from coal-tar which are midway between carbolic oil and anthracene oil. These are, in the first place, the fraction of coal-tar distilling directly between 240° and 270°, and, besides, from either side, the residues from the manufacture of carbolic acid, naphthalene, and anthracene. Practically every thing which cannot be used for any other purpose is run into the creosote-oil well. Since there are often very large stocks of this oil accumulating at the works, there must be correspondingly large store-tanks or wells, which need not be covered over, as the oil is not very volatile and the rainwater floats on the top of it, whilst the pumps take it away from the bottom. Still it is safer, as a precaution against fire, to cover up the tanks. At La Villette the creosote oil is kept in large upright cylindrical tanks, standing on brick pillars over a water-tank visible and accessible from all sides. Thus any leakages are noticed at once, and in any case the oil is prevented from penetrating into the ground. Where this is of no great consequence, the oil-tanks are mostly partially or entirely sunk in the ground. They are better if made of boiler-plate, than of brickwork set in cement.

According to Watson Smith it is advisable to fix a steam-pipe in the well, so that the naphthalene crystallizing out can be dissolved again before any large quantity is sent out.

Creosote oil (heavy oil, dead oil), when fresh, is light greenish-yellow, and strongly fluorescent, being rendered still more fluorescent

by the action of air and light. After some time it turns much darker and is bottle-green by reflected, dark red by transmitted light. As the distillation proceeds, it becomes darker and darker and more consistent. Its smell is extremely characteristic—unpleasant, almost nauseous; it is probably caused by sulphur compounds not yet isolated. It is as thick as oil, and at first has also an oily touch, but soon acts upon the skin by its acids. It is always heavier than water; the specific gravity of its last portions is 1·070.

The following bodies have been found in creosote oil:—naphthalene, methylnaphthalene, anthracene, phenanthrene, and the hydrocarbons coming in between these; phenol, cresol, &c.; aniline and all the other bases mentioned in Chapter III. (p. 150 *et seq.*). Only very few of the just mentioned substances are liquid, and it is certain that many more substances of a low fusing-point, as yet undiscovered, must exist in the liquid part of creosote oil.

We get an important insight into the nature of creosote oil (as well as anthracene oil) by the following results, obtained by Watson Smith with the distillation from Lancashire tar. Sample No. 1 was taken after 150 gallons had come over; No. 2 was a sample of the next 100 gallons; No. 3, of the next 100 gallons; No. 4, of the first "red oils;" No. 5, of the last oils.

No. 1 was of light colour, and on cooling was almost entirely solidified by the crystallization of naphthalene.

No. 2. Yellowish oil, with few crystals of naphthalene.

No. 3. Quite similar.

No. 4. Red oil, with but little deposit.

No. 5. Red oil, solidifying on cooling.

All contained a little water. Each of these samples was distilled, with the results given on p. 330, in percentages by volume (N signifies that, on cooling, naphthalene began to crystallize; O, that all remained liquid; A, that anthracene began to crystallize).

Heavy coal-tar oil has hitherto been put to the following uses:—

1st. Rectification, to obtain more valuable products.

2nd. Passing through red-hot tubes, to obtain illuminating-gas and more readily saleable hydrocarbons.

3rd. Pickling timber.

4th. Softening hard pitch.

5th. Preparation of varnishes.

Temperature.	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
	per cent.	per cent.	per cent.	per cent.	per cent.
Up to 180°	1·0	.....	6·6	1·0	2·7 O
„ 210	6·3 N	.....	4·7 N	2·0	1·1
„ 220	10·0	16·0 N	1·6	8·3 N	0·7
„ 230	12·0	5·5	7·6	2·0	0·7
„ 240	14·3	13·8	1·8	4·7	0·9
„ 250	13·3	9·8	8·3	.....O	3·3
„ 255	.....	.....	.....	.....	.....
„ 260	9·3	4·9 O	9·3	9·7	0·7
„ 270	7·0 O	8·9	1·6 O	12·0 A	1·8
„ 280	4·3 A	4·9 A	8·7	8·7	1·8 A
„ 290	3·7	3·5	6·6 A	5·4	1·8
„ 300	3·7	3·8	11·3	4·3	5·9
„ 310	3·7	2·1	4·5	3·0	12·0
„ 320	3·7	2·8	1·3	7·3	8·2
„ 330	.....	.....	.....		4·0
„ 335	.....	.....	.....		
„ 340	.....	2·8	.....	6·0	
„ 345	.....	.....	.....		
„ 350	.....	2·1	.....		
„ 360	.....	.....	1·6	18·0	
Above 360:					
Yellow crude anthracene	7·1	4·8	18·0	.....	34·0
Orange or red substance.	.....	1·8	4·3	5·3	16·0
	99·4	87·5	97·8	97·7	95·6
State of the pitch remaining behind on rectification	good.	very good.	half coked.	hard.	beginning to coke.
Totals.					
Crystallizing naphthalene oils	66·2	45·1	33·3	15·0	0
Not crystallizable oils ...	7·0	13·8	10·3	9·7	11·9
Anthracene oils	26·2	28·6	47·6	70·0	83·7

6th. Lubricating-oil, either in the crude state or after some preparation; also for preparing cheap mineral paints, in lieu of linseed-oil.

7th. Burning for heating-purposes.

8th. Burning for lampblack.

9th. Lighting.

10th. Carburetting gas.

11th. As an antiseptic.

Of these uses, the *softening of hard pitch* and the *preparation of varnishes* have been treated in pp. 246, 271, and 277. We need not dwell here upon the *burning for lampblack*, which in some places consumes a large portion of the heavy oil, since this is done exactly in the same way as described on p. 165 for tar itself, nor

upon the use of heavy oil as fuel, for which exactly the same apparatus are employed as described on p. 168 *et seq*. We shall therefore only describe the other uses of creosote oil.

Rectification of Heavy Oil.

This operation is only carried on in a few localities, *e. g.* in Scotland. Its object is, getting out as much as possible of the more valuable constituents. The oil is distilled in ordinary tar-stills; and the same kind of fractions are obtained: the result is a very small quantity of light oil, then a little carbolic oil, again the bulk of heavy oil, and at the close some pasty anthracene oils, which are added to those obtained in the direct distillation of the tar. The middle fraction, which preponderates, is used up in the manner previously detailed. No doubt this is the most thorough way of working up the heavy oils; but the expense of fuel, wear and tear, wages, and the unavoidable loss seem to deter most distillers from following it. Probably distillation in a vacuum would be the best plan.

Even more rarely will it pay to wash the heavy oils with sulphuric acid and caustic liquor before distilling them. The former takes up the basic bodies, but along with them a large quantity of other compounds (in the shape of sulphonic acids); the bases themselves are extremely difficult to separate (p. 155), and are employed for no technical purpose—except aniline, which is made much more cheaply from benzene than from heavy oil, the latter containing it ready formed, it is true, but only in minute quantity, so that it may be safely asserted that no aniline has ever been made directly from coal-tar for any practical purpose. The caustic-soda liquor dissolves the phenols; but for preparing pure carbolic acid the carbolic oil proper is much better adapted; still it sometimes pays to extract the phenols from heavy oil by an alkaline treatment.

It is stated by some that the heavy oil, after washing with acid and alkali, can be freed from the nauseous smell by being shaken up with 4 per cent. of its weight of ferrous sulphate, which removes certain sulphur compounds.

In the distillation of heavy oil, washed in the above manner, the first fraction (from 215° or 220°) will consist essentially of naphthalene, which, as well as the last fraction (containing anthracene), is collected by itself. The middle portion is adapted for lubricating-oil, for preparing paints, for illuminating-purposes (see

below), &c. Wurtz* recommends the following treatment. The heavy oil is distilled in boilers holding 1000–2000 litres; and the following are collected:—1st, the products below 120°, which go to crude benzol; 2nd, the products between 121° and 190°; 3rd, the residue, which goes back to the tar. The second fraction [between 121° and 190°?] is washed with acid and alkali, and is then sold for lubricating, or for pickling timber, or else it is converted into an illuminating-oil. For this purpose the naphthalene should be removed by treating with 10 per cent. concentrated sulphuric acid, then with water, then with 6 per cent. concentrated solution of caustic soda. The oil is now rectified; and the distillate is agitated with ferrous sulphate (compare above). The oil thus purified is sold as "huile sidérale"†.

Rohart (G.P. 14924) heats heavy coal-tar oil, crude petroleum, &c., mixed with lime, in a still for several hours, and then submits the mass to distillation.

Decomposition of Heavy Oil by Heat.

For a long time past attempts have been made, partly successfully, to utilize otherwise comparatively valueless oily residues by exposing them to a high degree of heat, *e. g.* passing them through red-hot tubes. Usually the main object was that of making illuminating-gas; but with this was associated the getting of more valuable oils. We have seen above (p. 90), that both benzol and anthracene can be obtained in this way from the heavy residues of petroleum, browncoal-tar, and wood-tar. Many chemists have worked in this direction, as Breitenlohner‡, Vohl § (who believes this process to be practicable), Walker and Smith ‖, and others. An apparatus specially constructed for the case in question was patented in 1861 by the Paris Gas Company ¶; it is represented in fig. 91. It consists of a set of cast-iron cylindrical retorts *a*,

* Matières colorantes, p. 33; Dictionn. de Chimie, i. p. 651.

† I have not been able to discover that any "huile sidérale," made in the manner described by Wurtz or in any similar manner from coal-tar oils, is sold anywhere. It is possible that in this case again there has been some confusion with paraffin oils; but even if it be otherwise, we can only say that the above process must have been given up long since, as at the present prices of illuminating-oils it could not possibly be remunerative.

‡ Dingler's Journal, clxvii. p. 378, clxxv. p. 392. § Ibid. clxxvii. p. 58.

‖ Wagner's Jahresb. 1867, p. 752.

¶ Technologiste, 1861, p. 145; Girard and Delaire, Dérivés de la houille, p. 20.

closed at one end and provided at the other end with a movable cover. About 12 inches from one end there is a partition *b*, 8 or 12 inches high, which prevents the oil from running towards the

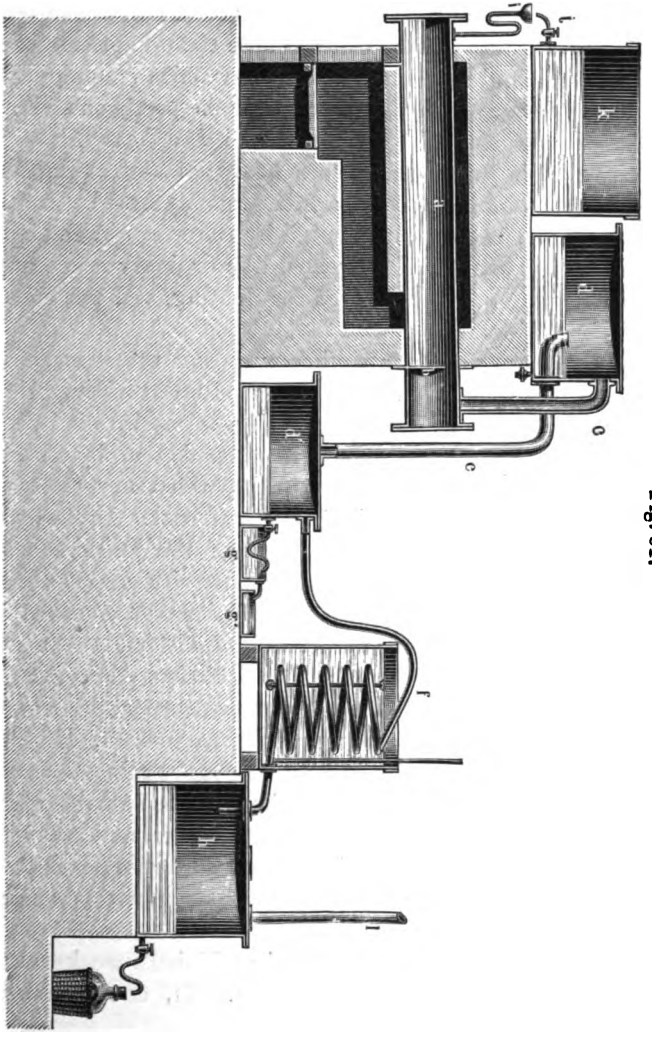


Fig. 91.

part not exposed to the fire. The space thus shut off communicates by an ascending pipe, *c*, with a receiver, *d*, which is connected by *e* with another receiver *d'*, equally intended for heavy

products of condensation: these are removed by the pipes *g g'*; whilst the vapours not yet condensed pass through the worm *f* and are collected in *h*. *l* carries away the incondensable gases. The heavy oil runs from the tank *k* through a tap, *j*, into the funnel *i*, and thence in a continuous stream into the retort *a*, previously brought to a red heat. There the oil spreads as far as the partition *b*, and is decomposed into graphite (remaining in the retort) and volatile products (passing over the partition and through the pipes into the receivers). In *d* and *d'* a heavy, tarry liquid condenses; it is mixed with more heavy oil and again run back into the retort [now-a-days it would probably first be worked for anthracene]. The liquid condensed by the worm *f*, and collected in *h*, is rich in benzol, and is treated like ordinary crude naphtha. The gas escaping at *l* is employed for lighting, and was considered the principal product.

Behrens* employed for a similar purpose a retort made of fire-bricks, heated from below. It was heated up to a very bright red heat; and a continuous jet of heavy oil was run into it by a swan-neck pipe. The volatile products were condensed by an ordinary hydraulic main and by very wide pipes, which nevertheless were frequently choked up with naphthalene and soot. In the hydraulic main (at the base of the furnace) most of the undecomposed oil was condensed; the remainder, together with naphthalene and the more volatile hydrocarbons newly formed, condensed in the cooling-pipes. In this way the heavy oil yielded on an average 2 per cent. benzene and toluene, and a little xylene and higher homologues. Below and above the temperature above mentioned less of the more volatile hydrocarbons was formed. In the former case but little heavy oil was decomposed†; in the latter the benzene was converted into naphthalene. In the furthest part of the condensing-apparatus naphthalene, benzene, and toluene were collected. The graphite remaining on the furnace-bed could be obtained in large pieces, and was valuable for producing high temperatures.

Of course the apparatus employed at Nobel's works, at Baku, for decomposing petroleum residues (p. 92), could be used for creosote oil as well.

* Dingler's Journal, ccviii. p. 361.

† Hence the cast-iron retorts patented by the Paris Gas Company cannot have stood a very long time, as they would have to be heated too high.

G. E. Davis's proposal of converting all the distillates from tar, except naphthalene and anthracene, into gas, as described p. 255 *et seq.*, may be mentioned in this connexion as well.

Formerly it would rarely have paid to convert tar-oils into gas; at present the price of creosote oil would be no obstacle to that, but it is very doubtful whether there is anything in it at all; comp. L. T. Wright, p. 256.

According to J. Young, heavy paraffin oils can be converted into light ones by heating them in strong iron boilers under a pressure of 1½ atmosphere. Possibly this would apply also to heavy coal-tar oils; but evidently nothing can be said as to the probable cost, yield, and so forth.

Employment of Heavy Oils as Lubricants.

This can be rationally done only after removing the phenols (acids), which promote friction. Naphthalene also will hardly be favourable to lubrication. But the mixture, hitherto very little known, of non-solidifying oils, which come before and along with anthracene, is really a lubricant, at least after proper treatment, and this sort of grease is pretty extensively used at collieries, &c., although the heavy paraffin and petroleum oils and rosin oil are far superior lubricants, and are now-a-days cheap enough to make the employment of coal-tar oils superfluous.

In order to prepare the latter for this purpose, the phenols (commonly called "acids") must be removed. This would be done effectually by the treatment mentioned on p. 331; but as this is mostly too expensive, the cartgrease-manufacturers treat the oils with lime, similarly to rosin oils, with which they are generally mixed. Thenius* prescribes gradually adding to a hundredweight of crude rosin oil, contained in a retort, 56 lb. of slaked lime, and heating, with agitation, till the whole is dissolved, then distil for an hour, condensing the vapours. The mass is now allowed to settle, and the clear portion is run off. On the other hand, 1½ cwt. of dry slaked lime is mixed in an open pan with ½ cwt. of rosin-oil and ½ cwt. of heavy coal-tar oil freed from acids; the mass is stirred and heated till it is quite homogeneous, and is then allowed to cool while being constantly agitated. Of each of the two mixtures thus prepared ½ cwt. is taken; they are mixed up in a pan; and, with constant stirring, a third mixture is added,

* Verwerthung des Steinkohlentheers, p. 82.

consisting of 23 lb. of melted ozokerite, ½ cwt. of heavy coal-tar oil free from acids, and ½ cwt. of heavy rosin oil. The latter mixture is added when it has cooled down to some extent, but before it has solidified. It may be coloured yellow with a few pounds of turmeric, or blackish blue by lampblack.

Thenius also describes another kind of cartgrease, made of a mixture of a tallow soap, fish-oil potash soap, and coal-tar oil.

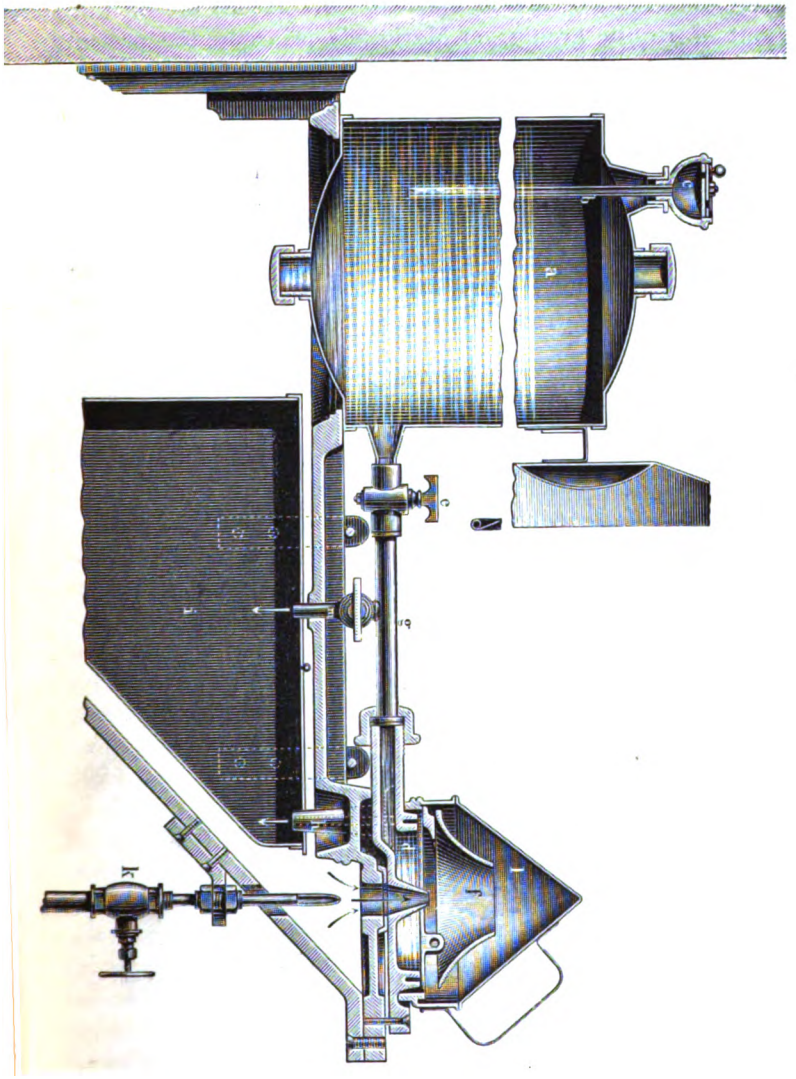
Dumoulin and Coutelle prepare lubricating-oil by stirring up 2 cwt. of creosote oil, 11 gallons of water, 2 lb. of bleaching-powder, 2 lb. of soda ash, and 1 lb. of manganese, settling 24 hours, decanting the clear liquid, distilling it, and mixing the distillate with one fourth of its weight of rosin oil: this treatment is to remove the "gummy" part of the tar-oils and to make them inodorous. Or else the oil may be distilled before adding the ingredients.

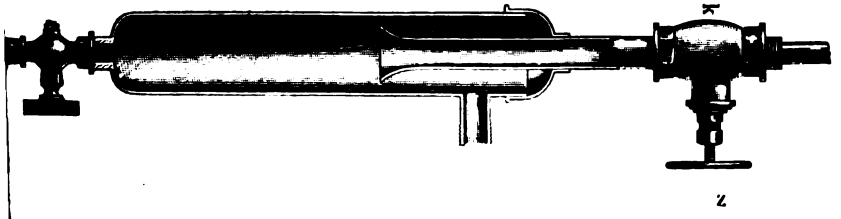
Employment of Creosote Oil for Lighting.

This has long been done in the construction of harbours, railways, &c., where the smoke was of no consequence. But this burning in open pans is a most wasteful, crude sort of illumination. The just mentioned process of Dumoulin and Coutelle was intended to make creosote oil fit for lighting even dwelling-rooms; but that degree of success is very doubtful. In order to get a proper lighting-effect, it is indispensable to introduce a jet of air, which prevents the formation of black smoke and burns the soot. Hence every thing depends upon the construction of the *lamps*. One of the best lamps for this purpose is the steam-jet lamp of Hartmann and Lucke*, shown in figs. 92 and 93. The steam-jet serves not merely to convey the oxygen necessary for combustion, but also to decompose the carbon compounds, thus preventing the formation of soot and producing an intense light. This lamp can of course be employed for any cheap petroleum or tar-oils, but is specially intended for ordinary creosote oil; it does not require a mechanical blast, but may be placed wherever steam can be had, and is thus principally adapted for lighting large factory workshops, yards, &c., but not for places which require a less intense and more divided source of light.

In the vessel *a*, filled with oil, is suspended the air-supply pipe *b*, ending at the top in a funnel, *c*, provided with a slide to

* German patent, No. 9195, Aug. 9, 1879.





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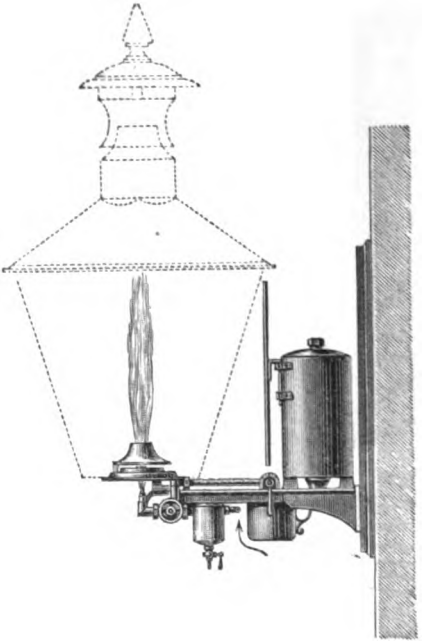
regulate the supply of air to the vessel *a*. Hence the oil must flow out of *a* quite evenly, on Mariotte's principle, the pressure being constant. It flows through the cock *e* and the pipe *g* into the dish *d* (which must be mounted in a perfectly horizontal position), where it is lighted and then covered with the funnel *f*: as the oil is difficult to light, it is first covered with a little petroleum. Steam, first dried in the apparatus *k* (fig. 93), is now, very slowly, admitted through the conical opening in the dish *d*. As soon as the oil burns equally all over the dish, which is brought about by regulating the steam-supply, the lamp requires no more attention. If by a wrong position of the slide at *c* the dish is

Fig. 94.



supplied with more oil than can be burnt, the superfluous part overflows into the annular channel round the dish and through the tube *h* into the vessel *i*. At first it is best to let it overflow; afterwards, when the oil has got hot, its supply is regulated so that the inner part of the dish always remains full. To put out the lamp the cock *e* is shut (so that no more oil flows into the

dish), the steam is shut off by the cock *k*, and the flame is extinguished by putting on the funnel-shaped cover *l*. The oil remaining in *d* and *g* is run into *i* by opening the tap *m*. This is a threeway cock, which either conveys the oil to the burner or else discharges it into the vessel *i*.

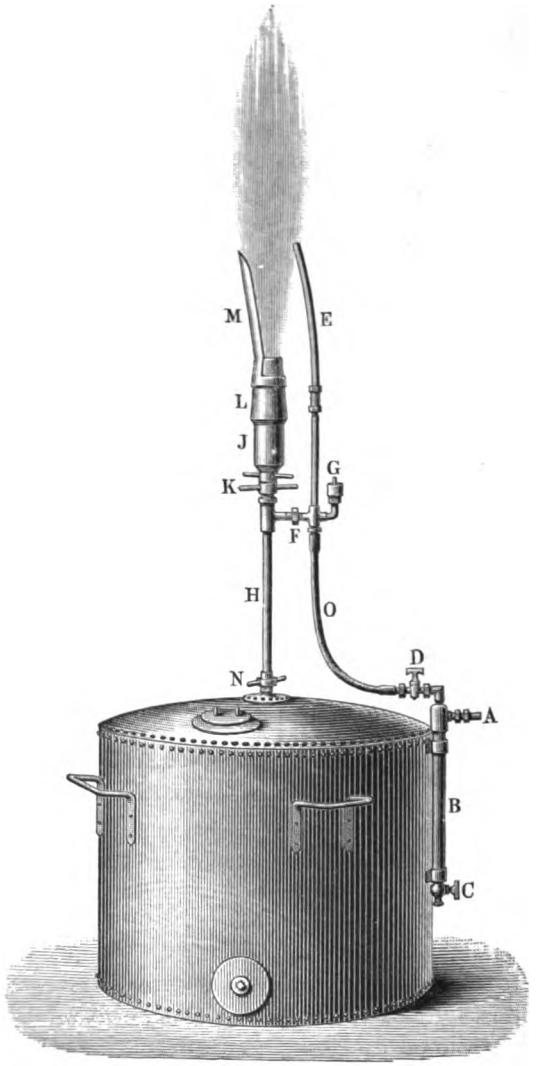
The steam admitted underneath the dish *d* acts mechanically by forcing the air necessary for combustion into the flame, and also aspirating the air from without through the openings beneath the funnel *f*. The steam also acts chemically upon the hydrocarbons, forming a gaseous mixture which, on combustion, produces an extremely brilliant light and no soot. This is not attained by ordinary lamps, because in them, when enough air is admitted, the flame becomes hotter but not more luminous. The steam should be as dry as possible; and the condensed water must be allowed to run away.

Thus the tar-oil burns without wick or chimney, preferably in very large glass lamps with reflectors. Such a lamp gives a light of 20 ordinary gas-lights or 180 standard candles, with an hourly consumption of about 2¼ lb. of tar-oil. The oil-vessel holds about 7 gallons, so as to suffice for the longest winter nights. The lamps need no cleaning or repairing.

The most recent form of this lamp is shown in fig. 94, $\frac{1}{12}$ natural size; this shape costs £5 including package, the glass lamp £4. Where the carriage does not make the oil too dear, this light is much cheaper than gas-light.

Another apparatus for the same purpose has been patented by Messrs. Lyle and Hannay (67 Great Clyde Street, Glasgow), under the name of the "Lucigen." I owe the description of it to the kindness of Mr. S. B. Boulton. It consists of an oil-tank or reservoir (fig. 95), fitted with a special burner at the top of a tube H, which can be made to any length. Into this reservoir compressed air is introduced by an india-rubber pipe, this material being used to make the lucigen portable. On the compressed air being let into the tank at A (B is a moisture-trap, C a blow-off cock), it forces the oil up through an internal tube, and, escaping at the same time through D, O, and E, with the oil in the burner J and combustion-chamber L, produces a spray which is set on fire. M is a wind-guard, K and N regulating jam-nuts, G a safety-valve. The pressure at which the air is forced into the accumulator is about 15 lb.; and this is sufficient to supply the

Fig. 95.



whole of the lights. A light of about 2000 candle-power is given by the "lucigen." The flame is large, and the light well diffused, and the eyes are not dazzled by it. It is claimed by the patentees that the "lucigen" is much more distributive in quality than the

electric light, and that it does not cast such deep shadows; also that it is much cheaper, alike in cost and maintenance, than either gas or electric light. It can be produced by either air or steam at a nominal expenditure of power, and it does not require any neat adjustment of machinery. The oil used in the lucigen is the refuse of chemical- and gas-works; and about one gallon per hour is consumed. Owing to the application of pressure, the "lucigen," when burning, emits a sound resembling steam blowing off. This, in a confined building, would naturally be very disagreeable; but in the open air the hissing noise emitted is not very annoying. There is scarcely any smoke from the light; and the smell of the consumed oil is not offensive. The lucigen burns equally well under heavy rain or spray. It does not need any lantern, and has no parts which can be damaged by rough usage.

The employment of creosote oil for *carburetting gas* will be discussed later on, along with that of other tar-oils (Chap. XI.).

As an *antiseptic*, creosote oil is but exceptionally used; for this purpose either crude tar or else its phenols by themselves are justly preferred. Dusart* asserts, however, that precisely the portion distilling between 210° and 300°, when freed from excess of naphthalene, acts energetically in preventing the further putrefaction, and destroying the smell, of fæcal matters, even in fractions of 1 per cent. This agrees with the observations made in pickling timber (see below).

Creosoted stakes in vineyards are asserted to keep out the *Phylloxera* (Polyt. Notizblatt, 1886, p. 304); but this does not seem to be a certainty.

Employment of Creosote Oil for Pickling Timber.

The preservation of timber, more especially railway-sleepers, telegraph-poles, piles used for harbour-piers, and so forth, is an industry of very considerable magnitude, and one intimately associated with that of coal-tar distilling, inasmuch as by far the largest part of the oils distilled from coal-tar is employed for this purpose, and as we can trace the first development of tar-distilling to the demand sprung up for such oils consequent upon the introduction of Bethell's process (1838).

The history of timber-preserving in general, and that of the

* Compt. Rend. lxxix. p. 229.

"creosoting" process in particular, has been given in several treatises, of which especially that by Mr. S. B. Boulton ("On the Antiseptic Treatment of Timber," Proc. Inst. Civ. Eng. 1883–84, vol. 78. p. iv) contains a great deal of original matter; the same subject is also treated in Adolf Mayer's 'Chemische Technologie des Holzes' (Braunschweig, 1872), Buresch's 'Der Schutz des Holzes' (2nd ed., Dresden, 1880), and Heinzerling's 'Der Conservirung des Holzes' (Halle, 1885). To those sources we refer for a description of the technical part of creosoting, which does not come within our domain, and to more detailed statements upon this subject in general.

Tar and pitch were used for painting or smearing wood in the remotest antiquity; special instances of preserving timber from decay are related in connection with the platform on which stood that wonder of the world, the statue of Zeus by Phidias, at Olympia, and with the famous wooden statue of Diana at Ephesus (Boulton, p. 5). The preservation of the Egyptian mummies may to a great extent be placed in the same category. But we must take a wide step in history before we get to any wide-spread application of antiseptics for wood. Apart from a few isolated trials with various antiseptics made during the eighteenth century, we find practically nothing done in this line till the beginning of the present century, although the records of the British Patent Office contain lists of almost every conceivable antiseptic from the year 1768 (Boulton, p. 8). But it is since the birth and growth of the railway system that the antiseptic treatment of timber has received its most important development. By the year 1838 the four systems of timber-preserving which alone are employed now were fairly before the public, and competing for the favour of engineers, namely:—(1) Corrosive sublimate, known since 1705, again introduced by J. H. Kyan; (2) sulphate of copper, known since 1767, principally introduced by Boucherie; (3) chloride of zinc, known since 1815, patented again by Sir William Burnett; and, lastly, (4) heavy oil of tar, afterwards called creosote oil, by John Bethell.

We shall, of course, occupy ourselves only with the last-mentioned process, which, moreover, has far outstripped the other three in importance, and in England has entirely extinguished its rivals. Vegetable tars, or extracts from the same, were used for timber-preserving, both in England and America, as early as 1756

(Boulton, p. 10). The first to mention the products of the distillation of gas-tar for impregnating timber was Franz Moll (British Patent, No. 6983, Jan. 1836). He proposed to employ, at the commencement of the operation, the oils lighter than water, which he called "Eupion," and afterwards the heavier oils, which he called "Kreosot." Both names were taken from Reichenbach's investigation on the products obtainable from wood-tar, as it was not known at that time what fundamental difference exists in the composition of wood-tar and coal-tar. Real creosote, in Reichenbach's sense, does not occur in coal-tar; but the phenol contained in the latter was for a long time confounded with Reichenbach's creosote. Moll's process, so far as the application of light oil was concerned, was manifestly unpractical; but the stimulus was now given for employing the products from coal-tar in that line, and in 1838 followed the practical introduction of the process by Mr. John Bethell. The words "creosote" and "creosoting," now generally used in this connection, are thus due to Franz Moll; they do not occur in Bethell's patent, which contains a list of no less than eighteen various substances, mixtures or solutions, oleaginous, bituminous, and of metallic salts. Amongst them is a mixture consisting of coal-tar, thinned with from one third to one half of its quantity of dead oil distilled from coal-tar; and as late as 1849 Bethell's licenses mention the admixture of gas-tar. In those times inspectors frequently refused to allow the dead oils to be used without being thickened with tar (Boulton, p. 14), as it was not understood that the pitch was only an impediment to the injection. Very soon after, this must have been recognized. The dead oils came into use alone; and there crept into the specifications the contradictory prescriptions that the wood was to be creosoted according to Bethell's patent, but that the creosote was to be free from adulteration with coal-tar.

The apparatus now universally employed for impregnating timber, both with creosote oil and chloride of zinc, was first suggested by Bréant, director of the Paris Mint, in 1831, who employed it for injecting linseed-oil and resin. The principle of Bréant's process was adopted by J. Bethell, and greatly improved by him and H. P. Burt. Their apparatus, as it was constructed more than thirty years ago, has been adopted everywhere in all its essential features, and is minutely described in the above-mentioned treatises. It consists of a very strong, horizontal, wrought-

iron boiler, 6 or 7 feet in diameter, and 30 to 60 feet long, $\frac{3}{8}$ inch thick. The timber is placed on iron bogie-frames, which are run upon rails into the cylinder, whose front is then firmly closed by a cover. The air is now exhausted till the air-gauge indicates about $\frac{1}{6}$ or $\frac{1}{8}$ of an atmosphere; communication is now opened by a cock with a tank holding the creosote oil, heated to a temperature of about 50°, at which it should be perfectly fluid. The oil at once rushes into the vacuum and deeply penetrates into the pores of the wood, whilst otherwise the air contained in them would pertinaciously resist the entrance of the oil. When no more oil is sucked up, a force-pump is started, which presses more oil into the cylinder, till a pressure of 8 or 10 atmospheres has been obtained. This is kept up for several hours; and the wood in this operation absorbs on an average nearly a gallon per cubic foot.

The plan of injecting creosote oils or similar substances in a state of vapour, which has been several times tried (Lukin 1812, Franz Moll 1836, Bethell 1864, &c.), could not possibly answer. Timber is weakened by exposure to a temperature much exceeding 120°, and is seriously injured at 150°; but the boiling-point of creosote oils ranges from 200° to about 370°. Hence its vapours can only be injected into wood under such conditions of temperature and pressure as will destroy the value of the timber; and experience has proved this to be the case. Nor has the application of superheated steam, passed through creosote oils, met with much more success (Boulton, pp. 30, 31, and below).

One difficulty of the creosoting process is the *presence of moisture* in the timber to be preserved. In the fresh-cut state, or as it is taken out of the timber-ponds, it is not in a fit condition for creosoting, and must be stacked first for from four to six months. Many methods have been tried for artificially drying the timber, in order to do away with the necessity of long stacking, which is extremely cumbersome or even impossible when piles &c. have to be sawn from larger logs, for immediate use in harbour works &c.; but they have all been abandoned, as, if the heat applied is really efficient in driving off the water, the woody fibre is sure to be injured in the process. Vohl* made a proposal which, if it were successful, would obviate the difficulty, by converting the creosote from an oily into an aqueous fluid, namely adding enough

* Dingler's Journal, vol. cxvii. p. 448.

solution of caustic soda to the creosote to make it miscible with water, impregnating the timber with this liquid, and ultimately "fixing" the creosote with a dilute solution of ferrous sulphate. But as this process was evidently never carried out on a manufacturing scale, nothing further can be stated about it.

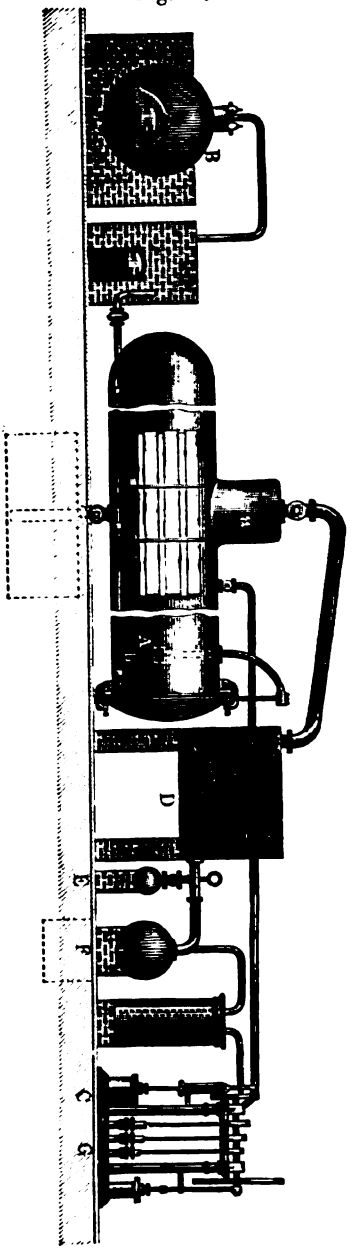
Another way out of the difficulty is to apply the creosote oil in a heated state, so that the water contained in the timber evaporates during the operation. A process founded upon this principle, but evidently imperfect in other respects, was invented by Pelton, and, according to a report made by Ott in 1874*, seems to have been largely employed in America at that period. It consisted in placing the timber, in the green state, in iron cylinders, covering it up with creosote oil and heating this for some time up to 100° or 110°, until the water was evaporated, and running in fresh cold oil. This causes the hot oil, already contained in the cylinder, to penetrate into the pores of the wood, a partial vacuum being caused by the cooling. The apparatus is figured and described in detail in the place quoted. It is very doubtful whether in this way the impregnation will be thorough; the very imperfect vacuum, and the absence of pressure at the finish, make this most unlikely. Pelton's process does not seem to have been very successful, for, according to a communication from Mr. S. B. Boulton, a committee of the American Society of Civil Engineers, in a report on the preservation of timber, presented and accepted at the Annual Meeting on the 25th June, 1885, does not mention Pelton's method among the many different processes described.

The object in quest is, however, completely attained by S. B. Boulton's process (B. P. No. 1854, of 1879). The timber is placed in the ordinary high-pressure creosoting cylinder (A, fig. 96), which is provided with a somewhat high dome, *a*. After the air has been exhausted in the usual way, the creosote is introduced through the pipe *b* at a temperature a little above 100°; but it is not allowed to rise quite to the top, so that the dome *a* is always kept empty, and the creosote is not drawn through the exhaust-pipe. The boiler B serves to heat up the creosote. The exhausting process is continued, by means of the pump C, until all the moisture contained in the pores of the timber has been vaporized by the heat of the creosote oil, and has been drawn away in the

* Wagner's Jahresbericht, 1874, p. 959.

state of vapour by the air-pump. As the temperature employed is much below the boiling-point of creosote, this liquid is not turned into vapour. The aqueous vapour is drawn through the dome *a*, is condensed by passing through the worm D, and the water is collected in the receiving-tanks E F, where the quantity extracted can be measured. The timber may be introduced quite wet; the water it contains is replaced by creosote, as much as 50 gallons per load of timber, without ever subjecting the wood to a dry heat. The process of injection can then be completed by means of the pressure-pumps G in the usual manner.

Fig. 96.



Boulton's process involves a slight additional cost and a few more hours for dealing with very wet timber, but not so much time and money as is required for stoving the timber, apart from the risk of deterioration incurred thereby; while for drying by stacking the timber six months, the interest and the value of the place occupied must be set off against the cost of the new process.

A process patented by Blythe, of Bordeaux (G. P. 10,423), essentially consists in injecting superheated steam into creosote oil, and allowing the mixed vapours of steam and creosote oil to act upon the wood contained in a closed boiler. The process has been extensively used in France, but with very unsatisfactory

results *. A sleeper which, according to the process usually followed in Germany, would take up 18 kilos. of creosote oil, absorbs only 11 kilos. in Blythe's process.

The German process, as carried out in the various large establishments of Jul. Rütgers, is as follows:—The sleepers are exposed in stoves to a temperature gradually raised to 130° C.; and are thus treated for at least four hours, until no more aqueous vapour is given off and the sleepers are uniformly heated. The sleepers are introduced while hot, being left on the same bogie, into the creosoting cylinder. After this has been closed air-tight, a vacuum at least as low as 55 millim. (=2 inches) mercury is produced within 30 minutes, and is kept up another 30 minutes. The cylinder is now placed in communication with the tank holding the warmed-up creosote oil, and, after being filled with it, is brought under a pressure of at least 6¾ atmospheres for upwards of one hour. Beech-wood sleepers should be either stove-dried or steamed in as fresh a state as possible, before the sap has begun to ferment. Stoving is difficult, because beech-wood has a tendency to split; it is therefore preferable to steam the timber till the temperature exceeds 100° even in the interior, and to remove the sap during the same process by lixiviation. When the pickling is to be performed by aqueous solutions, the steamed sleepers are best submitted directly to the impregnating process; but in the case of tar-oils, the timber must be first air-dried, which in spring or summer takes two or three months. Well-prepared and properly impregnated beech-wood sleepers do not suffer in comparison with those made of any other description of wood. The wood is impregnated all through; it remains hard and tough; and the bolts hold quite fast in it, as has been proved many times with rails which had been in use for a long time.

Rütgers sometimes applies a mixture of creosote and chloride of zinc.

Chaligny and Guyot-Sionnest have constructed *a travelling apparatus for pickling timber*, mounted upon two railway-trucks, which enables the pickling operation to be carried on at every railway station (Armengaud's 'Publication Industrielle,' 1884–85, vol. xxx. p. 295; Dingler's Polyt. Journal, vol. cclx. p. 75).

* Comp. Claus, Wagner-Fischer's Jahresb. d. chem. Techn. 1883, p. 1202, where a good many interesting details are given on the results of different methods of pickling timber.

Such apparatus, of their own construction, is also employed by Messrs. Burt, Boulton, and Haywood in their French business.

The creosote treatment is also applied to sails, ship's ropes, fishers' nets, &c., and protects these better than the usual tarring. The objects are first "tanned" by treating them with a dilute solution of glue and then with a bath of tanner's bark. Thus glue is precipitated within the vegetable fibre, which is now enabled to fix the creosote oil in the subsequent treatment, and retain it even in sea-water.

The advantages of pickling wood with tar-oils, or "creosoting," are both chemical and mechanical. The principal chemical action of coal-tar creosote was formerly ascribed to its "acids," *i. e.* the phenols, which certainly coagulate albumen, and consequently render animal life impossible. This, along with the now universal assumption that putrefactive decay can only occur in the presence of microscopic organisms, whose vital process is an indispensable condition of it, would by itself explain why timber impregnated with phenol cannot decay, provided that the phenol is not removed again by washing &c. Hence the value of creosoting-oils would be parallel with their percentage of phenols. But this opinion is generally contradicted now, and it is held that the "indifferent oils" participate essentially in the preservative action of coal-tar creosote. In any case the last-mentioned oils play a principal part in the *mechanical* effects of creosote oil, which are no doubt very important. The oil, being forcibly drawn into the wood by a vacuum and then driven in by high pressure, closes up all pores and, as it were, agglutinates all the parts so that no water can penetrate, without which those organisms cannot develop and the wood cannot decay. Even larger insects and other vermin are kept away by the smell of creosoted wood.

There are many undoubted instances of creosoted timber having successfully resisted even the redoubted *Teredo navalis* during a long series of years; but there are also cases of failure, sometimes in the same waters where the successful specimens have occurred. The failure is caused, either by the outer or creosoted part of the wood having been broken or cut off by the workmen in the process of construction, so that the worm could get into the inside of the timber; or by creosoting the wood in the wet state or imperfectly; or by employing creosote which is too thin, light, or volatile. Wood intended to resist marine insects should receive a heavier

dose of creosote, and is better employed in the round state than squared, because the sap-wood more readily absorbs the creosote than the heart-wood, and thus forms a protecting girdle against the worm. (Private communication from Mr. S. B. Boulton.)

It has long been disputed what part is played by the *naphthalene* in creosote oil. We know that it occurs abundantly therein, and crystallizes out on the cooling of the first fraction of this oil. Its quantity is increased by the residue from working the light oils for benzols, phenols, &c., which is extremely rich in naphthalene, going to the creosote oil. This, as it arrives at the creosoting-works, is often quite pasty with naphthalene. In the pickling process the oil is heated to 50°, so that the naphthalene is dissolved; and only on the cooling of the pickled wood does it crystallize again, among the other constituents of the oil, the coagulated albumen, &c. It was formerly believed that this was injurious to the preservation of wood, perhaps by the naphthalene volatilizing and leaving empty spaces which might be filled with moisture and become breeding-places for putrefactive organisms. Hence several creosoting-works have fixed a maximum for the naphthalene, which causes great inconvenience to the tar-distiller, since very much more naphthalene is produced than can as yet be consumed.

But it seems that the objection to naphthalene in creosoting is quite unfounded. In the first place, naphthalene itself is undoubtedly a disinfectant and prevents the development of lower organisms. Secondly, as has been proved by Dr. C. Meymott Tidy*, the total loss by evaporation of naphthalene is very small, and takes place almost exclusively during the first day or two after the wood has come out of the creosoting-apparatus. During the first and second day some naphthalene volatilizes from the surface of the timber; but after this there is no more loss of weight, and the interior of the wood is quite unchanged. According to Dr. Tidy the naphthalene is useful both chemically and physically; it cannot possibly do any harm; and the condition that creosote oil should be free from it seems quite uncalled for.

The following different requirements are made by some English and foreign creosoting-works:—

* In an official (unpublished) report kindly placed at my disposal by Dr. Tidy; compare later on his report of 1883.

Specification made by ...	Dr. Letheby.	Great Western Railway Co.	Chemin de fer de l'Est (France).	Chemin de fer de l'Ouest (France).	Chemin de fer de l'Etat Belge.
Spec. grav....	1·045–1·055 at 60° F., but as nearly as possible at 1·050.	1·045–1·055 at 60° F.	1·030 at 35° C.		
Deposit when cold.	Should not deposit any naphthalene at 40° F.	Should not deposit more than 30 per cent. at 40° F.	.....	.....	Not above 30 per cent. deposit (temperature not stated).
Yield of coal-tar acids.	5 per cent. crude carbolic acid and other coal - tar acids.	10 per cent. acids, of which 5 per cent. crude carbolic acid.	8 per cent. phenol.	5 per cent. phenol.	
Heat and quantity of distillate.	Should not yield less than 90 per cent. at 600° F.	Not less than 90 per cent. at 600° F.*	.....	.....	One third should distil at 200°–250°, two thirds above 250° C.
Heat and liquidity.	.....	.....	Should be perfectly liquid at 35° C.		
Further requirements.	.....	.....	.....	Should be of "first quality."	

The following Table † shows the general character of different descriptions of creosote-oils. The samples under A were the whole runnings of heavy oils distilled from samples of tar obtained from twenty different Metropolitan gas-works. The samples under B were produced at the Beckton tar-works, and represent oils from which portions of the green oils and naphthalene were excluded; they are hence rich in tar-acids and rather less volatile than A. The liquefying-point of the B samples ranged from 36°·7–32°·8 C., and the point of turbidity on cooling from 31°·1–28°·3. The samples in series C are country creosotes, analyzed by L. Archbutt. All were completely fluid at 32° and many at 15°·6. The sample yielding 72 per cent. of distillate and 13·5 of tar-acids was the

* This requirement has been dropped since 1882.

† From Allen's Comm. Organ. Anal. 2nd edit. vol. ii. p. 555.

product of special treatment. The samples in series C are probably somewhat richer in tar-acids than the generality of country oils:—

	Spec Grav. at 32° C.	Percentage of distillate below 315° C.	Percentage of tar-acids from distillate.
A. Heavy London oils: highest ...	1·075	79	8·0
" " " lowest ...	1·048	60	3·0
Average of 20 samples	1·0588	71·5	5·6
B. Partial runnings from London oils: highest	.....	91	10·2
Ditto, lowest	.....	78	8·2
Average of 20 samples	.....	82·8	9·15
C. English country oils: highest ...	1·056	90	24·0
" " " lowest ...	1·024	72	13·5
Average of 18 samples	1·0335	81·8	18·6

The creosote oils made in London and from tar made of Newcastle coal generally are richest in naphthalene and high-boiling constituents, and contain but a moderate percentage of tar-acids. "Country oils," or oils from the Midland district, are lighter, thinner, and more volatile than "London oils"; they usually contain less naphthalene and more tar-acids. Scotch oils, which are largely derived from cannel coal, are still thinner and more volatile, and sometimes lighter than water.

The present state of the important question as to what is the best quality of coal-tar oil for creosoting purposes is very clearly elucidated in the following memoir, for which I am indebted to the kindness of Mr. S. B. Boulton:—

"So long as scientific opinion remained unsettled as to the true causes of putrefaction, the choice of substances for its artificial prevention was of necessity more or less empirical. Liebig's theory of 'Eremecausis' was more philosophical than many of the previous attempts to solve the problem; it was nevertheless in contradiction with the idea that the fermentation and decay of animal or vegetable matter is caused by living organisms. He held that the processes of decomposition might be prevented by the application of various substances. But his theory offers no explanation of the *modus operandi* of the antidotes, and consequently it affords no sure guide as to their selection.

"To Liebig's theory there came to be superadded, somehow or

other, a prevailing belief that the putrefaction of animal and vegetable tissues could be permanently prevented by coagulating the albumen which they contained.

"But the question assumed an entirely different aspect with the development of the modern germ theory. As clearly stated by Pasteur, this theory affirms that, without the presence of living germs, the phenomena of organic decomposition do not declare themselves, and that these germs are the veritable agents of the decomposition. Further than this, various kinds of fermentation have, as we know, been distinctly traced to the action of distinct living organisms, each of which can be recognized, propagated, and relied upon to produce its especial kind of fermentation, as in yeast, vinegar, beer, wine, &c. Other organisms, pathogenic to living animals, have been discovered, and their methods of propagation and attack are subjects of absorbing interest and investigation.

"At last, therefore, we have distinct and reliable indications as to the nature of the substances which should be employed to retard or prevent organic decomposition. These antidotes must be *antiseptics*, i. e. they must either be capable of killing the hostile organisms, or they must produce such an environment of the bodies to be preserved as to prevent the development therein of these agents of destruction. I make use of the terms '*germicides*' and '*germ-excluders*' as characterizing these two properties.

"Meanwhile, what has become of the albumen-coagulation theory? I have had occasion recently to allude to the fact, that the most perfect coagulation by heat does not prevent the decomposition of albumen. An egg hard-boiled will, upon exposure to the weather, become in a short time a mass of corruption. The experiments of Herr F. Boillat, in the laboratory of Professor Nencki at Berne, prove that when albumen is coagulated by the most powerful antiseptics, the protection against decomposition is not permanent. Albuminates formed with solutions of chloride of zinc, sulphate of copper, corrosive sublimate, and carbolic acid were subsequently washed with water and exposed to the atmosphere at the ordinary temperature. All the albuminates developed micro-organisms, at periods varying from 2 to 45 days, and all of them putrefied after from 6 to 60 days, showing that antiseptics, which are of themselves soluble in water and volatile in air, are removed from their albuminates by the action of water and air.

Corrosive sublimate lasted longest, and carbolic acid was the least stable; the latter was completely washed out by water from its albuminate, and the albumen which had been treated with it began to decompose in 48 hours.

"These results, which perfectly agree with a mass of practical experience accumulated during a long series of years, throw further light upon the choice of antiseptics. Where immediate and not permanent results are required for the treatment of wounds, for the disinfection of sick-chambers, and for hygienic purposes in general, the solubility and the volatility of the antiseptics are frequently of advantage rather than otherwise. But for timber exposed to the atmosphere and to moisture it is apparent that we must not rely upon the coagulation-theory.

"It is for this reason that various timber-preserving processes, based upon the application of solutions of salts of metals, after obtaining considerable popularity, owing to their success during limited periods of probation, have ceased to be employed after more prolonged experience. For the same reason oily or bituminous antiseptics, when injected into timber, have been found to be more permanently successful, as they resist moisture and fill up the pores of the wood with substances inimical to the development of destructive organisms.

"Here again, however, certain oils, such as petroleum and others, have failed, owing to their volatility. And with regard to the cresote oils, which have been the most successful of all the antiseptics used for the preservation of timber, we shall find that the experience summarized in the preceding observations is especially applicable to the various bodies contained in the coal-tar distillates, and to the just appreciation of their relative value.

"The creosote oils had achieved a great practical success, say, from 1838 to 1860, without much chemical research having been employed upon them; and up to 1865 it was not usual to prescribe any form of analysis in creosote specifications. When, however, the value of carbolic acid began to be recognized, it was not astonishing that it should have been considered for a time as the most important factor of the success of cresote oils, more especially as the heavier portions of these oils had been but little studied, and were considered 'inert' for wood-preserving purposes. But later and exhaustive researches by a great number of chemists of the highest authority have altered these views. Carbolic acid is

known to be rapidly volatile in air and soluble in water. Its antiseptic action is rapid, but its combinations with animal and vegetable matter are not stable, so that, on exposure to the air, its protective influence speedily ceases. It has been said (*vide suprà*) that water will remove it from albumen which has been coagulated by it, after which the albumen becomes putrid. Dr. Koch has found that, in combination with oils, it does not exhibit any antiseptic action.

"Carbolic acid is contained in the lighter and more volatile portions of the creosote oils, amongst the earlier runnings from the tar-still. On the other hand, the value of the heavier and later runnings of these oils has now been recognized; they are necessarily the least volatile portions, they are impervious to the action of water, and they contain a number of valuable antiseptics, such as acridine, cryptidine, &c. They also contain tar-acids, or homologues of tar-acids, which are less volatile and less soluble in water than carbolic acid or cresylic acid.

"As regards naphthalene, which is found in considerable quantities in many samples of creosote oil, it is now known to be an exceedingly useful antiseptic, less energetic in its immediate action than carbolic acid, but much less volatile. As it forms deposits of a somewhat solid character at ordinary temperatures, it has been at times considered to act as an impediment to the injection of the oils into timber. But as all properly-conducted creosoting operations are now carried on at a temperature of at least 50° C., naphthalene is thereby rendered perfectly fluid, and can be thoroughly injected without the slightest difficulty. The after-solidification within the pores of the wood tends to resist the exudation of the more fluid portions of the oils, and the incursion of water and of micro-organisms.

"Practical experiments upon timber, and the experience of many years, entirely confirm the foregoing results of chemical research. Some of the most powerful antiseptics have not proved to be the most durable timber-preserving agents. Thus corrosive sublimate does not produce the same permanent results as the heavy oils of tar, and it completely fails with timber placed in water. With respect to the creosote oils themselves, experience shows the following results:—

"1. Carbolic acid is removed from creosote oils by repeated washings with water.

"2. When timber is injected with creosote oils containing carbolic acid, the latter invariably disappears, generally within twelve months.

"3. Numerous samples of creosote oils have had their lighter portions, containing all the carbolic acid, separated from the heavier portions, containing no carbolic acid. Wood-shavings have been impregnated with these separated portions, and subjected to putrifying influences during several years. The shavings prepared with the heaviest oils were always found to be perfectly sound; whilst those prepared with the lightest oils, which had contained the carbolic acid, were attacked by decay.

"4. Numerous specimens of creosoted timber which have been found to be perfectly sound after being used as railway sleepers, fencing, &c., for periods varying from sixteen to thirty-two years, have been carefully analyzed at different times and by different investigators.

"By all these analyses either no carbolic acid has been detected, or else such infinitesimally small quantities as to have no practical value. But the successful timber is always found to contain the heavier and less volatile portions of the oils, the greater bulk of which is composed of substances not distilling under 300° C. Acridine and cryptidine are found in many of the specimens, and naphthalene in most of them, the latter sometimes in considerable volume.

"What has been stated in the preceding remarks as to carbolic acid may be also applied, almost entirely, to cresylic acid—the exception being that the latter body is somewhat less volatile than the former.

"Chemical research and practical experience alike point to the course of selecting antiseptics in strict accordance with the special circumstances under which they are to be used. We inject timber with antiseptics in order that, when exposed to the atmosphere and to the action of water, it may be preserved for a prolonged series of years. It is evident therefore that the antiseptics chosen for this special purpose should neither be too volatile at ordinary temperatures nor too soluble in water.

"For a detailed account of research and experiments on the foregoing subject by a great number of authorities, together with a history of the timber-preserving processes, see my paper on 'The

Antiseptic Treatment of Timber,' read at the Institution of Civil Engineers of London, 6th May, 1884.

"S. B. BOULTON,
"Assoc. Inst. Civil Engineers; Member of the
"Society of Chemical Industry."

Mr. Boulton's opinions practically coincide with those expressed in the

Report of Dr. C. MEYMOTT TIDY, M.B., F.C.S., *on the Description of Creosote best suited for Creosoting Timber*
(made to the Directors of the Gas-Light and Coke Company, August 1883),

of which we reproduce the more important portions in a somewhat abridged form :—

"The advantages to be derived from the creosoting process are of a *threefold* nature, and I give them in what appears to me to be the order of their importance :—

"1st. *A physical action.* A very greatly increased solidity is effected by choking up the pores, thus agglutinating the whole mass of the wood into a more or less solid block. Apart from its rendering the wood more solid, this physical action is important in preventing the subsequent absorption of moisture.

"2nd. *A physiological action.* The smell of the creosote imparted to the wood prevents germinal life, well known to be destructive to timber, from being developed within it. Seeing that the preservation of timber has been effected by such materials as chloride of zinc, sulphate of copper, &c., with greater or less success, and that the action of these bodies must be mainly, although I admit not entirely, dependent on their toxic properties, this physiological action is one of importance. It must be remembered, moreover, that creosote has the advantage of a well-marked smell, which odour most of the lower animals dislike. In this respect it is superior to the other bodies I have named.

"Further, it is worth pointing out that all the constituents of the coal-tar, and not the tar-acids only, have a more or less well-marked tarry odour.

"3rd. *A chemical action.* Respecting the chemical action, I would draw attention to the fact that tar-acids are not only anti-

septic, but that they possess the power of coagulating albumen. It is to this latter action that I shall have to refer later on in this Report, as playing an important part, in my opinion, in the preservation of the timber.

"Now, the two following questions arise:—(1st) Upon what constituents of the creosote does its value specially depend, and what are the relative values of its different constituents? (2nd) If there be constituents in the creosote, which of themselves possess no special value, do they in any respect lessen the activity of the valuable constituents?

"The importance of considering the precise value of the several constituents of creosote arises as follows:—

"Speaking generally, creosote may be divided into two classes, London and Country creosotes. By London creosote we mean the creosote derived from the tars of the London gasworks, the east coast generally, and from the gasworks of towns such as Southampton, Brighton, &c., where the coal employed is Newcastle coal. So far as I am able to learn, the larger proportion of the creosote produced in England is of this character. The two creosotes, however, being very different in their composition, it becomes important to consider them separately.

"*The London creosote* has a somewhat high specific gravity, and contains a comparatively large percentage of naphthalene, and a small percentage (*i. e.* less than 10 per cent.) of tar-acids. Further, it contains a considerable quantity of the heavier portions of the oil, that is, of those portions not volatile at a temperature below 600° F. (316° C.).

"*The Country creosote*, on the other hand, has a less specific gravity, and is considerably more fluid than London creosote. It contains considerably less naphthalene than the London creosote, a larger total percentage of tar-acids, and a smaller percentage of the heavier portions of the oil present.

"The real question I have had in view in this inquiry being country creosotes *v.* London creosotes, it became necessary to inquire the relative values of the heavier portions of the oil, of the naphthalene, and of the tar-acids in creosoting.

"The tar-acids, in the first instance, effect the coagulation of the albumen of the wood-sap. This coagulated albumen mixes with the naphthalene of the creosote, which, so soon as the temperature becomes sufficiently reduced, is redeposited, and forms, along with

the heavier portions of the oil, a solid magma within the pores and fibres of the wood. That this formation of a solid magma actually occurs, I have convinced myself by numerous microscopic examinations of creosoted timbers.

"The success of the process, therefore, being presumably assisted by the coagulation of the albumen, the question arises, *What quantity of tar-acids is necessary to effect this object?*

"There is very little doubt in my mind that 2 or 3 per cent. of tar-acids would amply suffice to effect this coagulation of the sap albumen.

"We are now led to consider if any value, and, if any, what value, is to be ascribed to the tar-acids beyond that needed to effect the coagulation of the albumen.

"I am far from prepared to say they are otherwise entirely valueless. Still it is a remarkable fact which I have over and over again verified, that in the timbers that have been creosoted for a considerable time (say a year) very small quantities indeed (if any) of free tar-acids are to be found.

"I have upon this point instituted a series of examinations of sleepers obtained from independent sources, and of ages varying from one to twenty years; and it is a fact worth noting that, within a very short time after a sleeper has been in use, the tar-acids appear to be entirely dissipated *.

"Seeing, however, that the life of a sleeper is by no means so limited, the facts I have mentioned suffice to show that the action of the tar-acids *per se* cannot have any very great or permanently preservative influence in creosoting.

"I admit it was natural to suppose that bodies commonly regarded as powerfully antiseptic should have been the active agents in the process. Further, I must admit that it was with such view I commenced this inquiry. My recent investigations, however, have clearly shown that the value of the tar-acids in the creosoting process has been greatly overestimated.

"I am convinced that, so long as the quantity of carbolic acid present in the creosote is sufficient to coagulate the albumen of the wood-sap, it is also sufficient for practical purposes.

"I have now to consider the value of the *naphthalene*.

"I am disposed to think that this body is of infinitely greater

* "This Report was written some time before the appearance of Mr. Greville Williams's paper. My own results, I may say, are in entire accord with his."

value than at first sight appears. Admitting that, as an antiseptic, it is inferior to the tar-acids, nevertheless, so far as preservative action alone is concerned, it must not be supposed to be inoperative. Its special value, however, consists in helping to render the wood solid.

"But it may be said, granting this to be the case, naphthalene is so volatile that the heat of the sun, especially the intense heat of an Indian climate, would soon drive the whole of it off. It is true that on exposing a block of creosoted timber in an oven to a temperature of 54°·5 C. (130° F.), and this may be taken to be an extreme tropical heat, the door of the oven, after a short time, shows conclusively that some of the naphthalene in the sleeper has undergone volatilization by the heat applied.

"I would, however, direct attention to the following experiment:—

"I exposed a large block of creosoted timber (accurately weighed) to a temperature of 65°·5 C. (150° F.). On weighing this at the end of twenty-four hours, I found it to have lost 1200 grains. On exposing the same block to the same temperature for another twenty-four hours, it lost 135 grains, whilst on continuing the exposure for a third twenty-four hours, it lost only 15 grains. After this the loss was practically *nil.*

"I now planed off about ¼ inch of the block I had already heated. This done, I again exposed it to a heat of 54°·5 C. (130° F.) for twenty-four hours, during which time it lost 1150 grains. The loss on the second day was less than 100 grains, whilst on succeeding days the loss was practically *nil.*

"The surface of the wood was again planed off, and similar experiments repeated a third time, with almost identical results.

"From numerous microscopical examinations of the timber, and from the experiments I have described, I consider that I am justified in drawing the following conclusions *re naphthalene*:—

"1st. That supposing, for the sake of argument, naphthalene possesses no great antiseptic power, nevertheless it acts beneficially by clogging up the pores of the wood, forming a more or less solid magma with the coagulated albumen. In this way it assists the physical part of the creosoting process, upon which the preservation of the timber materially depends.

"2nd. That although a certain quantity of naphthalene would undoubtedly be volatilized by a tropical heat, nevertheless the

loss would be practically limited to the *surface* of the timber, and would be complete a day or two after exposure, the naphthalene in the deeper parts of the wood remaining fixed by incorporation with the albumen coagulated by the action of the tar-acids.

"3rd. That inasmuch as the naphthalene cannot injure the action of the tar-acids, or other constituents of the creosote, and is itself a positive benefit to the process, there is not only no object in requiring that the oil used for creosoting should be free from naphthalene, but that it would be unadvisable to demand such freedom.

"There are many other facts that in my judgment corroborate the views I have expressed. Thus I am given to understand that, during the twelve years after the process of creosoting was first introduced into India, the whole of the sleepers were prepared with heavy London creosote (that is, a creosote highly charged with naphthalene), with the occasional admixture of a small quantity of country oil for the purpose of dilution.

"It is perfectly certain, further, that it was on account of the good results so obtained that creosoting became a process of acknowledged utility.

"So far as I can learn, it was not until the country oils became more extensively used that any complaints respecting the inefficiency of the process arose. From independent inquiries, I think there is the strongest possible reason to believe that the sleepers that proved unsatisfactory had been prepared with country, and not with London oil.

"Nothing has impressed me more strongly in the course of these inquiries than the value of the *heavy oils* present in the creosote, that is, of the oils that do not distil over under 600° (316° C.). Of a certain antiseptic power, and very difficult of volatilization, they are, I believe, bodies of great value in the oil employed in the creosoting process."

Taking into consideration the above arguments, Dr. Tidy recommended a specification for creosote, which we here give in this form, amended by himself in 1885:—

"*Dr. Tidy's Specification for Creosote* (*as amended in* 1885).

"1. That the creosote shall be completely liquid at a temperature of 100° F. [38° C.], no deposit afterwards taking place until the oil registers a temperature of 95° F. [35° C.].

"2. That the creosote shall contain at least 25 per cent. of constituents that do not distil over at a temperature of 600° F. [316° C.].

"3. That, tested by the process hereafter to be described, the creosote shall yield a total of 8 per cent. of tar-acids.

"4. That it shall contain no admixture of bone-oil, shale-oil, or of any substance not obtained from the distillation of coal-tar; and that the first 25 per cent. of the distillate shall have a specific gravity greater than that of water.

"Process to be adopted for determining the Coal-tar Acids.

"1. 100 c. c. of the well-mixed creosote is to be distilled at a temperature of 600 F. until no further distillate comes over. The distillate so obtained is to be mixed and well shaken in a stoppered flask with 30 c. c. of a solution of caustic soda, of specific gravity 1200. The mixture is then to be heated. This done, the stopper is to be replaced in the flask, and the hot mixture again shaken vigorously for at least a minute.

Fig. 97.

"The contents of the flask are now to be poured into a separating funnel (fig. 97), and the soda-solution drawn off. The creosote is to be heated a second and a third time in a similar manner with the caustic soda solution, except that only 20 c. c. of the soda solution shall be used for the second and third extractions, instead of 30 c. c., as in the first extraction.

"2. The three soda solutions are now to be mixed together. *When cold* any particles of creosote are to be got rid of by means of a separating funnel. This done, the solution to be thoroughly boiled, in order to expel the last traces of creosote present in the solution. The mixture is then to be allowed to cool. When cold, dilute sulphuric acid (1 of acid to 3 of water) is to be added (about 35 c. c. will be required) until the solution becomes slightly acid to litmus. The whole is then to be poured into a separating funnel, and allowed to stand until perfectly cold, and the tar-acids well separated.

"3. The tar-acids are now to be dissolved in 20 c. c. of the caustic-soda solution (specific gravity 1200) and 10 c. c. of water. The mixture is then to be boiled and filtered through a funnel fitted with a plug of asbestos. The asbestos plug is to be washed

with not more than 5 c. c. of boiling water. The solution is to be allowed to cool *perfectly* in a 100 c. c. measure. It is then to be rendered slightly acid with dilute sulphuric acid (1 to 3), (10 c. c. will probably be found sufficient for this purpose). The whole is again allowed to stand *for two hours* until *perfectly cold*, when the percentage of the tar-acids is to be read off.

"*Process to be adopted in estimating the quantity of Distillate.*

"The operation is to be conducted in a retort (fitted with a thermometer), and heated with the naked flame of a Bunsen burner. The heat applied is to be gradually raised to 600° F., and continued at that temperature until no further matters distil over. The distillation of the 100 c. c. should be completed within half an hour."

The above has been entirely upheld by a new Report, made by Dr. Tidy to the Gas-Light and Coke Company on Feb. 11, 1885, in reply to a paper by Dr. Voelcker and to the specification suggested by that gentleman. We now append the reasons given by Dr. Tidy for some of the above details :—

"1. The omission of any clause specifying the specific gravity of the creosote to be used. I have done this advisedly, because of the extreme difficulty in taking the gravity of creosote at normal temperatures with the 1000 grain bottle, and the practical uselessness in my judgment of employing a hydrometer for the purpose. If it be considered necessary to introduce a specific-gravity clause, I would suggest that the gravity be between 1040 and 1065, water being 1000. I am of opinion, however, that for practical purposes, a specific-gravity clause is altogether unnecessary.

"2. Believing strongly as I do in the value of those constituents of the oil that are the most difficult to volatilize, I have deemed it right to suggest a clause to the effect that the creosote shall contain at least 25 per cent. of matters that distil over above 600° F.

"3. I have made a large number of experiments as to the best method by which the estimation of the tar-acids may be determined.

"I note—

"(*a*) That very slight differences in the strength of the solutions used, and in methods of manipulation, considerably influence the results obtained. I therefore deem it necessary that, as a part of

the specification, the process to be employed for estimating the acids should be exactly stated.

"(*b*) I have failed to discover any easy method of separating the carbolic from the other tar-acids. I have tried for this purpose numerous experiments, but with such unsatisfactory results that I have decided to recommend that the total quantity of tar-acids only should be stated. Further, the fact that as preservatives one kind of tar-acid is, so far as we know, as good as any other renders a further separation of the acids in my judgment unnecessary. My analyses of samples will show that, in fixing not less than 8 per cent. of total tar-acids, we obtain a fair index of the purity and genuineness of the creosote."

We conclude this chapter with

Sir F. Abel's Specification, January 2nd, 1884, for Creosote.

"The creosoting liquor is to be of the description known as heavy oil of tar obtained by the distillation of coal-tar, and consisting of that portion of the distillate which comes over between the temperature of about 350° F. (176° C.) and that of 760° F. (405° C.).

"The liquor must be free from admixture with any oil or other substance not obtainable from such distillate. It shall contain not less than 20 nor more than 30 per cent. of constituents that do not distil over at a temperature approaching 600° F. (316° C.).

"It must yield not less than 9 per cent. by volume of tar-acids when tested in accordance with the instructions annexed.

"The creosoting liquor must become completely fluid when raised to a temperature of 100° F. (38° C.), and exhibit no signs of any deposit on cooling down to a temperature of 90° F. (32½° C.).

"The specific gravity of the liquor must not be less than 1·035, and not more than 1·065 at a temperature of 90° F., as compared with water at 60° F.

"*Test for Creosoting Liquor.*

"1st. The liquor, if necessary, is to be warmed until it is perfectly fluid.

"A 100 c. c. is then to be placed in a glass retort of convenient size, and subjected to distillation until a temperature of nearly 600° F. is attained.

"The thermometer regulating the temperature must be so placed in the retort that at the commencement of the distillation the bulb of the thermometer is entirely immersed in the liquid, but not touching the bottom of the retort. The distillate should be collected in a stoppered glass bottle, having a capacity of about 200 c. c.

"2nd. The distillate is to be mixed with 20 c. c. of a solution of caustic soda (specific gravity 1·21), the mixture being shaken at intervals for a period of not less than three hours, and is then to be transferred to a burette provided with a glass tap, into which has previously been introduced a few drops of soda solution sufficient to fill the narrow space above the stopcock. The burette, with its contents, is then to be set aside for 12 hours, in a place sufficiently warm to keep the mixture fluid. The soda solution containing the tar-acids will then be found to have separated from the other portions of the creosoting liquor, occupying the lower portion of the burette, and should then be drawn off into a small glass flask, which should have a capacity of about 100 c. c., and be provided with a long narrow neck (divided into cubic centimetres) of sufficient length to be capable of holding the whole of the tar-acids afterwards separated. The liquor not acted upon by the soda-solution is to be returned to the bottle by inverting the burette. Ten c. c. of fresh soda-solution is then to be added, and the mixture again treated as before. The soda-solution from this second treatment, containing any further amount of tar-acids not extracted by the first treatment, is then to be added to the soda-solution first obtained in the long-neck flask. Sulphuric acid, dilute (1 vol. of oil of vitriol and 3 vols. of water), is now to be gradually introduced into the flask until a very slightly acid reaction is produced, the flask being kept cool. Then enough mercury is poured into the flask to drive all the tar-acids up into its neck, where their volume can be read off on the graduation.

"*Note.* If the creosoting-liquor is of an unusually thick consistency, it may be found necessary to subject it to a preliminary distillation which should be conducted as described at A; but the use of a thermometer is not necessary, as the distillation should be continued until nothing further comes over."

It will be seen that Abel's specification very nearly agrees with Tidy's, and that the separation of carbolic and cresylic acid by

fractional distillation of the tar-acids, formerly prescribed by Sir F. Abel, but objected to by me in the first edition of this treatise (p. 208) as quite illusory, has been dropped. Tidy's prescription of boiling the alkaline solution of the tar-acids, in order to expel any hydrocarbons, is, I think, quite called for; but then Abel requires 9 per cent. in lieu of 8 per cent., which will compensate for the impurities left by his treatment in the tar-acids.

The *tests made at the works* are mostly more simple than the above. The *density* is best ascertained at about 32°, when the oils are all fluid, by means of a hydrometer, or else by a specific-gravity bottle, which is allowed to cool down to 15°, when the stopper is pressed in tightly. The *liquefying-point* is found by placing some of the oil in a test-tube, inserting a thermometer and moving about in a warm-water bath; the *point of turbidity*, by allowing the whole to cool down. The *distillate up to* 315° is found by heating 100 c. c. in a 4-ounce retort by a small naked flame, protected by a tin cylinder. The thermometer ought just to touch the liquid remaining at the end. The distillation should last about thirty minutes. The *tar-acids* are usually estimated in the distillate by treating it twice with 30 and 15 c. c. of caustic-soda solution of spec. grav. 1·21, at a gentle heat, separating the oil by a tap-funnel, cooling down, adding 30 c. c. of dilute sulphuric acid (1 acid to 3 water, transferring to a graduated cylinder), allowing to *cool completely*, and reading off the volume of tar-acids separated (Messrs. Burt, Boulton, and Haywood).

If the *basic constituents* are to be estimated, the rules mentioned in Chapter III., p. 155, must be observed.

Carriage of Creosote Oil.

On a comparatively small scale creosote oil is conveyed in wooden casks, which are very liable to leak unless they have been previously washed with a solution of glue. On a larger scale exactly the same contrivances are employed as for tar itself, viz.:—for railway carriage, block waggons with cylindrical or angular wrought-iron tanks holding 8 or 9 tons; for water carriage (on rivers or canals), tank boats.

CHAPTER IX.

CARBOLIC ACID AND NAPHTHALENE.

Carbolic Acid (Phenol).

For some years after the preparation of carbolic acid became an industry it was found suitable not to work for that purpose the whole of the "light oil," but merely the last portion (that between sp. gr. 0·980 or 0·990 and 1·000). Since then the demand for carbolic acid has largely increased, and that for naphthalene has risen to a considerable extent. Consequently all the better factories manage their process so as to obtain a special fraction between that yielding the light hydrocarbons and the heavy oils, which is specially rich in phenols and naphthalene. We have certainly seen (p. 233 *et seq.*) that this fraction is not made everywhere exactly on the same principles; and its quality at one works will consequently differ a good deal from that at another; but this makes no difference in the manner of treating it to the best purpose, which we shall now describe.

The principle is always this:—Treating the oils with caustic-soda liquor, which dissolves the phenols (tar-acids); this solution is decomposed by mineral acids, and crude carbolic acid is obtained; the oil separated from the alkaline liquor is redistilled and yields naphthalene, along with other products. According to whether the fraction has been made sooner or later, the benzene homologues will have to be sought for or the contrary. The crude carbolic acid is partly employed in this state for disinfecting-purposes, and partly sold to those who work it for crystallized phenol, &c.

The following is the original process for preparing pure phenol,

by Laurent*, and is essentially identical in principle with that which is even now employed. The fraction of coal-tar distilling between 150° and 200° is treated with a hot saturated solution of caustic potash or soda, some solid powdered caustic potash or soda is added, and the mixture well agitated [just in this point, viz. employing solid caustic, the process differs from that now in use; probably at that time, in 1831, the tar did not contain so much naphthalene as now, because the cast-iron gas-retorts then used could not be worked at such a heat as the present fireclay ones; moreover, Laurent worked with a comparatively low-boiling fraction, poor in naphthalene]. The oil sets to a crystalline paste; the liquid portion is decanted, and the solid part is dissolved in warm water. Two layers are formed—a light oily one (which is removed), and a heavy watery one (which is saturated with sulphuric or hydrochloric acid). The oil which is formed in the latter process and found floating upon the acid liquid is digested with fused chloride of calcium and fractionally distilled. Thus a white oily substance is easily obtained, which on being slowly cooled yields beautiful crystals.

It has been attempted to cheapen Laurent's process by employing lime in lieu of potash or soda, boiling and strongly agitating. On settling, the neutral oils come to the surface and are removed by decantation; the lime-precipitate is decomposed by hydrochloric acid, and yields phenol. This simple and cheap process, however, does not give a good result; and the treatment with caustic soda is universally preferred, but with a much weaker solution than that prescribed by Laurent. At all events the preparation of perfectly pure crystallized carbolic acid is any thing but simple and easy. It is said that such acid was first made on a large scale by Sell, of Offenbach †; but in any case it was introduced into trade on a manufacturing-scale by the exertions of Crace Calvert and Charles Lowe, of Manchester, who for a considerable time had almost a monopoly of it. Nowadays it is made at other English as well as continental works.

* Ann. Chim. Phys. [3] iii. p. 95.

† According to a private communication from Mr. Brönner, of Frankfort, this gentleman as early as 1846 made so-called white limpid ("wasserhelles") creosote, which was frequently refused because in winter it solidified to a white crystalline mass! This was, of course, owing to the then general confusion between carbolic acid and the real, original "creosote" from beech-wood tar (comp. p. 137), which latter compound is never found in the solid state.

Experience has shown that carbolic acid proper (C_6H_6O) cannot very well be made from the creosote oils distilling above 240°. These always contain tar-acids, but mostly the higher homologues; and the latter are universally admitted to be of great importance in the process of preserving timber, being less soluble in water, and less volatile than carbolic and cresylic acids, so that it would seem wrong to remove them. We shall therefore not take the heavy oils into account for this purpose. On the other hand, if a "middle oil" has not been collected (from about 170°), in the working-up of the "light oil" (to be described in the next chapter), considerable quantities of residues rich in phenol and naphthalene are obtained; these are added to the "carbolic oil," and make it about equal to the "middle oil" of other works.

The following are examples of the composition of middle oils (from Stohmann-Kerl, vi. 1179):—

Distilling at	I.	II.	
100°	0	0	per cent.
100°–180°	14·1	9·2	„
180°–200°	41·5	35·2	„
200°–250°	38·7	19·2	„

Watson Smith gives the following results for "light oils" (really equal to "middle oils" from Wigan cannel-coal tar (compare p. 263):—

Distilling below	Oil of sp. gr. 1·000.	Oil of sp. gr. 1·019.	
170°	10	0	per cent.
180°	5	0	„
190°	12	5	„
200°	22	24	„
	49	29	„

Some recommend redistilling such oils *before* the alkaline treatment, receiving the fraction between 170° and 210° as crude carbolic oil, and running the residue to the creosote oil. But this will cause a considerable loss of phenols*, and it is much more advisable to treat the whole of the middle oils with *alkali*. Even by distilling in a still with a dephlegmator (see below), only part of the naphthalene can be separated from the crude oils; hence

* Watson Smith confirms this.

it is preferable to effect the first separation by the alkaline treatment. In any case it will be well to let the oil rest for some time, so that as much naphthalene as possible shall crystallize out and can be removed.

According to E. Waller*, in America the light oil is distilled at temperatures below 177°–220°; steam is passed through the distillate as long as it carries away any oils; the distillate ("rectified coal-tar naphtha") is worked for benzol, and the residue ("naphtha tailings") for phenol. If these short hints actually represent the American style of treating the first coal-tar fractions, it cannot be pronounced quite so rational as it might be.

First of all it should be ascertained how much alkali the oil requires. It is not necessary in this case to make a formal analytical estimation (of which we shall speak hereafter), but only to find the minimum quantity of alkali required for exhausting the oil. This need only be tested for roughly, in the following manner:—50 c. c. of the oil is put into a 100 c. c. graduated cylinder; and the soda solution is gradually added, shaking after each addition and allowing the liquids to separate. The dark-brown solution of sodium carbolate is distinct from the oil which may be above or below it. The volume of the oil is noted; and if on the next addition of alkali it is not lessened, the last addition must have been sufficient. From this is calculated the quantity of alkali to be used in actual manufacturing-work.

From what we have seen (p. 143 *et seq.*) respecting the behaviour of phenol and cresol with alkalis, we know, first, that true phenol is more easily soluble than its homologues, and hence requires a weaker lye; secondly, that a large excess of caustic liquor may reprecipitate the phenols. Still the margin is so large, that in regular manufacturing-work a test like that just described is hardly required, because there will be no very striking differences in the percentage of phenol. But where unknown oils have to be treated, such a test will have to be applied.

According to Behrens† an important manufacturing "secret" for making crystallized carbolic acid consists in treating the oil with a quantity of dilute soda solution, insufficient for dissolving all the tar-acids; in that case carbolic acid, being the strongest, is first taken up. If at all, this plan has not been pursued in the

* Chem. News, xliii. p. 150.

† Dingler's Journal, ccviii. p. 363.

first treatment of carbolic acid, as there is no certainty here about the quantity of alkali required; possibly it may have been done in the subsequent working-up of the crude carbolic acid. Those tar-distillers who only proceed as far as crude carbolic acid (and they are the great majority) find it to their interest to completely extract the phenols, and hence will not apply the above-mentioned process.

The following special prescription for the extraction of phenol was given by Charles Lowe, the first manufacturer of the purest crystallized carbolic acid*:—20 tons of gas-tar are introduced into a retort and distilled. The first 200 gallons of "light benzols" are of no use for the extraction of carbolic acid. When that amount of distillate has passed over, the next 600 gallons are collected separately. For each 200 gallons of these oils, having a density of 1·0 to 1·005, 30 gallons of caustic-soda solution of sp. gr. 1·34 are added after dilution to 150 gallons, and the oils are then agitated with the solution for two hours. The mixture is next allowed to settle for four hours, when the alkaline solution is drawn off and neutralized with sulphuric acid. The crude carbolic acid rises to the surface and is skimmed off, and is then allowed to settle in tanks for several days, after which it is ready for casking. The caustic soda used must be free from nitrates.

Here, as we see, rather dilute alkaline liquor is prescribed. In regard to this, the following points should be borne in mind. The less pure the oils, the weaker should be the caustic solution, if good phenol is aimed at. With crude benzol (which always contains some phenol) stronger caustic can be employed; and the phenol obtained will be still better, though less in quantity, than that from carbolic oil. For this reason some distillers do not begin the washing of crude benzol, as usual, with sulphuric acid, but with caustic-soda solution of sp. gr. about 1·200. In the case of "middle" or carbolic oil, such strong alkali would dissolve too much hydrocarbons, especially naphthalene, which would greatly impede the purification of carbolic acid, and might altogether prevent it from crystallizing. Moreover oils are dissolved which have a tendency to turn dark in the air, and thus spoil the phenol. Hence in this case weak alkaline liquors must be employed; and probably Lowe's prescription is more trustworthy than any other,

* From Allen's 'Commercial Organic Analysis,' 1st ed. p. 305.

since his interest is to obtain the best quality of crude carbolic acid from the tar-distillers.

Watson Smith takes 33 per cent. by volume of caustic liquor 18° or 19° Tw. for carbolic oil, or 40 per cent. by volume for light oil.

At a large English factory carbolic acid is extracted from all the light distillates, up to (of course not including) creosote oil, in the following manner:—The first runnings are treated with rather stronger caustic soda solution, viz. of sp. gr. 1·15, and in great excess. This is done previous to the washing with vitriol. The solution thus obtained, containing some carbolic acid along with a great deal of free soda, is mixed with a fresh quantity of somewhat weaker alkali, so that the sp. gr. comes down to 1·125. This liquor is now employed for treating the carbolic oil, at a temperature of 65°–77° C. The resulting solution of carbolate of soda is separated from the naphthalene oil floating on the top, and the latter dissolves also the impurities taken up by the caustic soda from the first runnings, which otherwise cause the carbolic acid, made from first runnings alone, to be of inferior quality. Thus, by simplifying the process, both the quantity and the quality of the carbolic acid are improved.

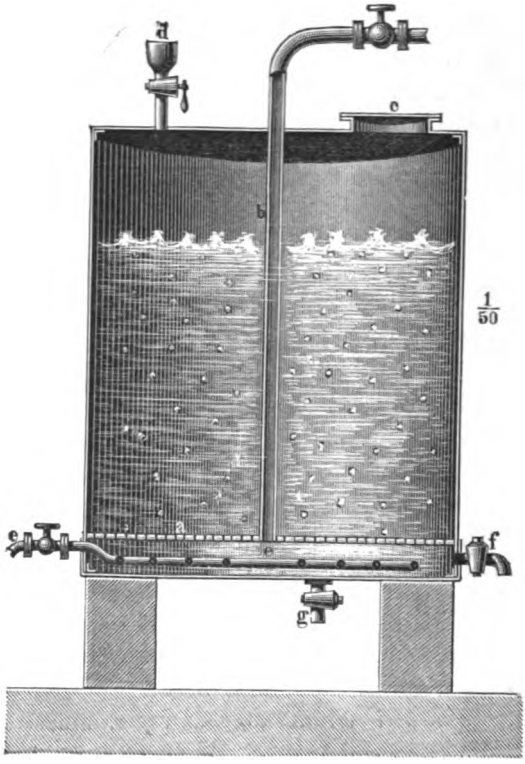
A large South-German manufacturer states* that he obtains crude carbolic acid (with 50 per cent. crystallizable acid) by employing caustic liquor of sp. gr. 1·26, steaming the solution, and decomposing the alkaline liquor by acid. He lays much stress upon the subsequent fractional distillation of the crude acid, but none upon the employment of weak alkaline liquor, or upon fractional saturation (p. 369). Where only crude carbolic acid is made, and no special conditions are imposed by the buyers, sometimes stronger alkaline liquors, up to 35° Baumé (=sp. gr. 1·32), are employed; but this must yield a product difficult to refine.

The mixing of carbolic oil and alkaline liquor must of course be done very thoroughly, and with gentle heating, say to 40° or 50°, by means of a steam-coil or jacket. Probably all larger works employ mechanical means for mixing. At some it is done by pumping both liquids continuously backwards and forwards from a lower tank into a higher one and *vice versâ*. At others they employ horizontal cylinders covered by a bad heat-conductor, with a longitudinal shaft and agitating-blades. Horizontal agitating-

* In a private communication to the author.

shafts have the drawback that they must pass through the sides of the vessel, in stuffing-boxes; but the agitation produced by them is more thorough than that produced by vertical apparatus. One of the best forms of the latter is that of a perforated piston going up and down*. We shall treat of mechanical mixers more in detail in the 11th chapter. At some places the agitation is effected by blowing in a current of air, divided by a cross of pipes with many

Fig. 98.



holes, or a perforated plate. This principle has the advantage of dispensing with all working parts within the liquid, and thus being equally applicable for acids and alkalis; the blowing can be performed by the same small blowing-engine which is employed at most tar-works for pumping the liquids by air-pressure. Fig. 98 shows this arrangement. *a* is a perforated false bottom, which

* Hübner, Dingler's Journal, cxlvi. p. 421.

serves for dividing the current of air, blown in through *b*, into numerous jets; *c*, man-hole; *d*, funnel and tap for charging with oil and alkali; *e*, steam-coil; *f*, discharge-cock a little above the bottom; *g*, another discharge-cock in the bottom itself. The air-blast must be so regulated that the liquid shall not be splashed about, but only made to well up thoroughly. A detailed paper on the application of compressed air for the pumping and mixing of liquids has been published by Ramdohr*.

According to Watson Smith, the oil and alkali are mixed up for an hour and a half; the mixture is then tested by mixing, in a 200 c.c. graduated cylinder, 140 c. c. of the alkaline liquor with 14 c. c. strong sulphuric acid, and allowing it to subside; unless at least 10 or 12 per cent. crude carbolic acid is found to collect at the top, the mixing should be continued.

The mixing-vessel for this purpose is always made of iron, usually wrought iron, which metal resists the liquor better than any other; the steam-coils, air-pipes, &c. are also made of iron. When mixing by an air-blast, the vessel should be only two-thirds full, on account of the frothing up. It is mostly closed by a wooden or iron cover, to minimize volatilization. According to the size of the works, the settling (which takes several hours) will either take place in the same vessel, or else the whole contents will be run into a special vessel, placed at a lower level, so that the mixer can be charged again at once. The settling-tank must have two (iron) discharge-cocks, one in the bottom itself, another in the side a little above the bottom. The unchanged oil always floats on the alkaline liquid, which sometimes doubles its bulk and is of intensely dark brown colour. First of all this liquid is run off by the bottom cock, which is closed as soon as any traces of oil appear. Now the upper cock is opened, through which oil entirely free from alkali can be drawn off, whilst between the two cocks a layer of both liquids remains, which is best left behind in the vessel and worked up with the next charge.

As pointed out by Watson Smith, the point at which the alkaline liquid is going to change for the oily one can be safely recognized by the turbid, milky appearance which sets in.

It is imperative to keep the alkaline liquid as pure as possible from the separated crude naphtha, because even a small admixture of the latter (especially of the naphthalene contained therein)

* Dingler's Journal, ccxvi. p. 158.

afterwards prevents the crystallization of the carbolic acid. Hence great care must be taken in settling and in drawing off.

The *oil drawn off from the solution of carbolate of soda* [crude naphtha] contains mostly a little of the higher homologues of benzene, but principally naphthalene and other indifferent bodies; also some of the impurities originally contained in the first runnings, if the soda solution has been previously employed for treating these (p. 371). If naphthalene is not wanted, this oil is run to the "light oil" (compare next chapter) and worked up therewith. Sometimes this does not pay, viz. when the original oil has been collected later on in the distillation; then the residues are run to the creosote oil. Where naphthalene is an object, this oil is by far the best raw material for it, as we shall see below.

The *liquor containing sodium carbolate*, to which is regularly added that obtained in the washing of benzol and light oil, is now mostly at once decomposed by acid. But some prefer to interpose a special treatment for the removal of impurities. Thus Vincent* adds to the liquor 5 or 6 times its bulk of boiling water, to precipitate the dissolved hydrocarbons. This should not be overdone (compare p. 143); and anyhow the success of this operation will depend upon the fact whether more or less concentrated alkali has been employed from the first. (Vincent starts with concentrated alkali.) Schnitzler† recommends, as extremely efficient, heating the dark liquid in a copper still over a strong fire till the distillate (consisting of water, naphthalene, oils, and phenol) turns milky; the thermometer will then stand at 170°. Most of the phenol remains with the soda as a mass solidifying on cooling. It is dissolved in water in the still itself, and is diluted to three times the original bulk. After some days a mud is deposited, from which the clear liquor is separated. The latter is decomposed by dilute sulphuric acid; and the phenol separated is distilled from a glass retort. After putting aside the water "coming over at first, colourless liquid phenol of honey-like (?) smell was obtained, which solidified on the addition of a small piece of calcium chloride, or a crystal of carbolic acid. The portions passing over last were faintly yellow, and contained more liquid parts. The crystals, after draining them with a Bunsen pump and pressing them between paper, remained white for months in a stoppered bottle in moderate day-

* Payen, Précis de Chimie industr. 6th ed. ii. p. 961.

† Dingler's Journal, ccxiv. p. 86.

light; in an open glass they soon turned pink, and at last deliquesced to a yellow-red liquid. The colour was evidently produced by particles of dust floating in the air" (? See below).

For the large scale Schnitzler recommends a wrought-iron still with a block-tin, lead, or copper worm, and to put a second delivery-tube lower down for use in the later stage of distillation. Insufficiently heated sodium carbolate yields yellow, unpleasantly smelling phenol; it is essential to completely remove the colouring impurities by evaporation or carbonization &c. An experiment with calcium carbonate did not succeed (perhaps because there was an excess of lime); the mass turned spongy, conducted the heat badly, and retained tarry matters and naphthalene.

Another purifying-process is described in Stohmann-Kerl's 'Chemistry'*. The crude sodium carbolate is run into open wood tubs, on the bottoms of which is laid a steam-coil perforated with many holes. The liquor is moderately warmed; and enough freshly prepared cream of lime is added to make the whole milky white. During this the mass is worked up with a wooden rake; and the heating is continued for 12 hours. After a few hours a skin appears on the surface, which gradually turns into a red foamy scum. It consists of the naphthalene left in the liquor, mixed with lime. It is carefully removed with a perforated wooden scoop, either at once, or at least after the liquor has cooled down. Thus all naphthalene, even to the last trace, can be removed; but it is most essential to keep the heat at the right point. The temperature must never rise so high that the liquid wells up strongly. Perhaps an insoluble compound of lime and naphthalene is formed; but the action of the lime may be only mechanical, the naphthalene being secreted from the alkaline liquor as it is diluted by the steam blown in. In any case the tubs must be left uncovered and must stand in an unheated room. When the naphthalene has been completely removed and the liquor has settled, it is carefully drawn off from the lime remaining at the bottom, and is decomposed by sulphuric acid.

From what I have heard on trustworthy authority, it seems to be sufficient but indispensable for obtaining good crude carbolic acid, free from dissolved or finely suspended hydrocarbons, a very slight admixture of which afterwards impedes the crystallization of phenol, if a current of steam is passed into the liquid,

* 3rd edition, vi. p. 1181.

contained in an iron still provided with a refrigerator, till a sample of the distillate is perfectly clear and bright, without any milkiness.

Now follows the *decomposition of the alkaline solution of phenols by mineral acid, and the separation of crude carbolic acid.* This operation is generally performed in a vessel lined with lead, which may be provided with a mechanical agitator; but in this case hand mixing is easy and simple. Iron vessels are acted upon too quickly. Sometimes this tank is covered over, so that any noxious gases escaping in decomposing the sodium phenate by acids can be conveyed under a fire and burned. The acid employed for the decomposition is mostly sulphuric acid. The solution of sodium sulphate resulting from this is probably never utilized as such; and the spontaneously crystallizing Glauber's salt is also of very small value*. If dilute caustic liquor and sulphuric acid of 140° Tw. be employed, but little will crystallize out spontaneously. Some tar-distillers take strong (170°) oil of vitriol; but this is worse than useless, as sulphophenols are formed, which in the subsequent distillation decompose and carry sulphurous acid into the carbolic acid. The addition of the vitriol must be cautiously done, to avoid strong heating, and is only continued till the reaction has become distinctly acid. The men can tell this from the change of colour, without applying litmus-paper. According to W atson Smith, 1000 gallons, treated with 400 gallons of caustic-soda solution of sp. gr. 1·090, require about 22½ gallons of sulphuric acid of sp. gr. 1·74.

It has been several times attempted to replace sulphuric acid by the acid refuse from washing the light tar-oils (Chap. XI.), after depriving it, by dilution with water, of most of its tarry parts. But it is still very impure; and its use for decomposing sodium phenate has been given up everywhere, as the saving of acid does not compensate for the contamination of the phenol. It is true that another motive was the desire to get rid of that acid refuse; but the proposal of E. Kopp, to combine the employment of this refuse acid for decomposing the sodium phenate with working-up the resulting solution for the alkaloids contained in coal-tar, could hardly be expected to meet with success, looking at the deterioration of the carbolic acid.

According to Watson Smith, in Lancashire even fresh sulphuric

* According to Watson Smith, the crystals always turn blue on standing in the air.

acid made from pyrites is not employed for this purpose but brimstone acid almost exclusively. [This is probably from an unfounded prejudice; for the reason, given in the Journal of the Society of Chemical Industry, 1882, p. 342, that pyrites acid discolours the sodium sulphate, cannot hold good here, as the value of the crystallized sodium sulphate is almost nil, and certainly much less than the difference in price between pyrites acid and brimstone acid; moreover the sodium-sulphate solution is nearly always run to waste.] He further mentions that attempts had been made, but unsuccessfully, to replace sulphuric acid by hydrochloric acid, which is cheaper [and causes less trouble by crystallizing salts]. The alleged reason of this failure is that chlorides of ammonium and organic bases are formed, which later on are decomposed and action upon the iron of the stills ensues; the ferric chloride distils over, and makes the carbolic acid dark and dirty. Ammonium sulphate produces no such consequences. Against these statements must be placed the fact that some of the best German works employ hydrochloric acid, and among them are those that turn out the very finest quality of white crystallized carbolic acid.

Lowe and Gill* propose decomposing the alkaline phenol solution by sulphurous acid. The aqueous solution of the bisulphite is either to be evaporated for crystallization, or employed for preparing sulphurous acid again. It is probable that this plan answers well; and the sulphurous acid would be obtained very cheaply by working up the "acid-tar" from the washing of crude naphtha (comp. this in Chapter X.).

In the place of strong acids, *carbonic acid* can be employed for decomposing sodium phenate. In Scotland this seems to have been done for some years†; Brönner‡, of Frankfort, had done it already many years ago. A patent has been taken out by Clift (B. P. 967, 1880) and another by Wischin (B. P. 3750, 1880) for exactly the same thing. If the decomposition can really be completed without wasting too much carbonic acid, there are considerable advantages gained by this process as against the employment of strong acids. In the former case the soda is not lost, as in the latter, but is recovered as carbonate and can be used over again after causticizing. There would not, as now, be a rather

* English patent, No. 1456, 1880.

† Mills, 'Destructive Distillation,' p. 17.

‡ Private communication to the author.

considerable amount of phenol lost, either dissolved or suspended in small drops, in the solution of sodium sulphate or chloride; for as the liquor is causticized and used over again, the phenol would be recovered. No washing of the phenol would be at all necessary, as the latter would retain no mineral acids, which probably give rise to the formation of traces of rosolic acid (p. 147), and thus turn the carbolic acid red. This, of course, presupposes that the carbonic acid itself is entirely free from stronger acids, which is hardly the case in the ordinary way of working, since even that made from coke or in lime-kilns is contaminated with sulphurous acid. It seems therefore necessary to wash the CO_2 most thoroughly with water, or else to produce it by the action of superheated steam on limestone in iron retorts. Lest too much of it should be wasted, it should be divided into numerous jets by a perforated false bottom or the like, and several vessels should be employed in rotation to utilize the gas methodically, so that the fresh gas (which in the case of lime-kiln gases contains from 25 to 30 per cent. CO_2 by volume) shall always be brought into contact with nearly saturated liquor, and the poorest gas with fresh liquor, on the same principle as that in accordance with which black ash is lixiviated. In this way it has been found possible on a manufacturing scale to completely decompose solutions of sodium sulphide by carbonic acid without employing an excess of the latter*. There would also be this advantage, that, as the carbonic acid need not in this case be free from oxygen, any fire-gases might be used, if well washed: oxygen even acts advantageously here (see below).

J. Hardman (B. P. 7079, 1885) runs the alkaline solution of the phenols down a coke tower, in which ascends impure carbonic acid, namely the gases from the manufacture of ammonium sulphate, after having been freed from sulphide of hydrogen by oxide of iron. This inventor also utilizes the suggestion (already contained in the first edition of this treatise, 1882) to re-causticize the alkaline carbonate formed, and thus save the 2 or 3 per cent. of tar-acids otherwise lost with the sodium-sulphate liquors.

Some experiments made in my laboratory by one of my students† seem to show that the separation of phenol from its

* This is described in detail in my Treatise on the Manufacture of Sulphuric Acid and Alkali (Van Voorst), vol. ii. p. 352.

† Chemiker Zeitung, 1883, p. 29.

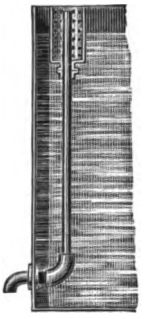
salts by means of carbonic acid is complete; but it should be stated that private communications have reached me, according to which the employment of CO_2 on the large scale has not been successful. It does not appear, however, that this point is altogether decided; and I have been informed that new attempts will be made to realize this reaction on a manufacturing scale.

Sulphuretted hydrogen has also been proposed for decomposing the carbolate of soda (Jane, Elland, and Steuart, B. P. 2469, 1883). Since the patent was annulled, owing to the failure of filing the final specification, there does not seem to be much in it.

After the separation of the crude carbolic acid, the solution of salt, if sulphuric acid has been employed, must be drawn off hot, lest it crystallize in the precipitating-tank. In the case of hydrochloric acid there is no such danger, and more time can be given for the solutions to clear, so that less phenol is lost with the solution of salt. The latter is drawn off by a tap in the bottom, which is shut the moment any carbolic acid appears, whereupon the latter can be drawn off in the pure state from another tap higher up (p. 373). It is preferable to leave the carbolic acid to itself for a day or two to clear, so that the salt-solution suspended in it may completely separate at the bottom: this can be done in a special settler. The longer the time given for the salt solution to separate from the carbolic acid, the better for the quality of the latter.

In many cases the crude carbolic acid is now sold as such; in other cases it is washed once or twice with water to remove the mineral acids—which, however, is never done completely, because the washings would carry away too much carbolic acid. In any case the washings should not be thrown away, but employed for dissolving the caustic soda. The washings are found floating *on the top* of the carbolic acid, and are run off best by a drop-siphon (fig. 99), which can be gradually turned down. This is much more convenient than a common siphon.

Fig. 99.



Sometimes the crude carbolic acid is previously *distilled* by the tar-distiller, in order to get it up to the requirements laid down by the buyers (compare below). In that case the fraction distilling between 175° and 205° or 210° is collected as

crude carbolic acid. The fraction below this goes to the light oil, the residue to the creosote oil.

Crude Carbolic Acid should have a specific gravity of 1·050–1·065 at 15°·5. In the presence of light tar-oils its sp. gr. is often only 1·040–1·045. It contains phenol, the different isomeric cresols, phlorol, xylenol, neutral tar-oils, naphthalene, empyreumatic substances of unknown character, and water. The processes for testing its percentage will be described later on.

Preparation of pure crystallized Carbolic Acid.*

We have already stated that this manufacture is rather difficult, and some of its details are still kept a secret. In the following I shall enumerate what has been published on this subject, together with some results obtained by Mr. Watson Smith and by myself.

Crude carbolic acid, as supplied by the tar-distillers, contains cresols, water, naphthalene, resinous matters, &c. The easiest to remove is the *water*; by mere distillation most of it is expelled at 100°; and the boiling-point then rises rapidly, so that at 180° anhydrous phenol passes over. Still more safely, the raw product, first freed from most of its water by distillation, is digested with fused calcium chloride and then drawn off from it (not distilled over it, since in that case the $CaCl_2$ would again give up some water). Bickerdike † recommends distilling over 1 or 2 per cent. dehydrated cupric sulphate, which can always be recovered. Exactly the same service is done by 1 or 2 per cent. of concentrated sulphuric acid (see below).

The *distillation* usually takes place in cast-iron or wrought-iron stills holding only 150–200 gallons, of moderate depth, so that the vapours are carried away more readily. The heating is mostly effected by a direct fire, with a protecting arch; but it can also be done by an oil-bath, or by superheated steam in a lead coil. Others recommend copper stills, which are especially adapted for the distillation over sulphuric acid, with or without potassium bichromate (see below). The stills are in every case provided with a thermometer, whose mercury vessel is placed opposite the vapour-delivery tube and whose scale projects outside. The worm is best made of zinc (see below).

* See, for its properties, p. 137 *et seqq.*

† Chemical News, xvi. p. 188.

Watson Smith recommends luting the man-hole cover with a paste of a solution of glue and partly slaked quicklime. I should prefer asbestos packing.

In distilling, the following fractions are made. First is collected what distils below 180°; this is mostly water and hydrocarbons floating on the top of it; but it already contains some phenol, and is hence kept in order to be redistilled. The second fraction, from 180° to 205°, is put aside for crystallization; the still-residue either goes to the creosote oil, or is rectified once more, in order to collect the distillate below 205°; or else it is once more treated with alkali &c.

The above-mentioned principal fraction is left to crystallize in a cool place (at about 8° or 10° for instance), in large funnel-shaped vessels with a tap below, through which afterwards the mother liquor can be drained away. The latter is a solution of phenol in cresol, and is redistilled. Its draining from the crystals may be facilitated by a centrifugal machine. The above low temperature will be obtained during the summer season sometimes by circulation of cold water, sometimes only by a freezing-mixture.

If this fraction should refuse to crystallize (which will happen if it contains too much cresol), it must be rectified and the distillates from 175° to 185°, from 185° to 195°, and from 195° to 205° collected separately. The first and last fractions are redistilled, when enough of them has accumulated; the middle fraction (from 185° to 195°), some of which is no doubt obtained again, is united with the former. It is evident that no general prescription can be given, but that the fractions, which may become very numerous, must be grouped according to their boiling-points, so as to separate the homologues and ultimately get the boiling-points to be constant within a few degrees, viz. 184–188° for carbolic acid and 200–203° for cresylic acid. The ordinary crystallized phenol boils at 186°; if the purest, boiling at 182°, is aimed at, the thermometer must be observed accordingly.

Instead of making such a complicated series of rectifications and groupings of the fractions, it is evident that the principle of *dephlegmation* or *separation* is the proper one to employ here as well as in the rectification of spirit of wine, or in that of benzol, where Mansfield employed it a generation ago. It consists in *partially* cooling the vapours, so that the less volatile bodies are condensed and flow back into the still. This principle can be applied in very

different ways. We shall see in Chapter XI. how this is done for benzol; here we will only describe the apparatus constructed by Girard for the separation of aniline and toluidine, which must be suitable for phenols as well, because their boiling-points very nearly agree with those of the amides. In fig. 100, *g* represents a still with discharge-pipe (*t*), man-hole (*h*), thermometer, vapour-delivery pipe (*a*), and a pipe (*b*) for running back the liquid that comes from the separator (*k*). This separator, formed of lead pipes, is placed in a trough, *i*, filled with pure phenol or with oil or paraffin, heated by a separate fire and covered by a lid in which is fixed a thermometer and a pipe, *d*, which, when phenol is employed, leads to a worm, *r'*, or, in the case of oil or paraffin, into a chimney. The separator itself is connected by *f* with another worm, *r*.

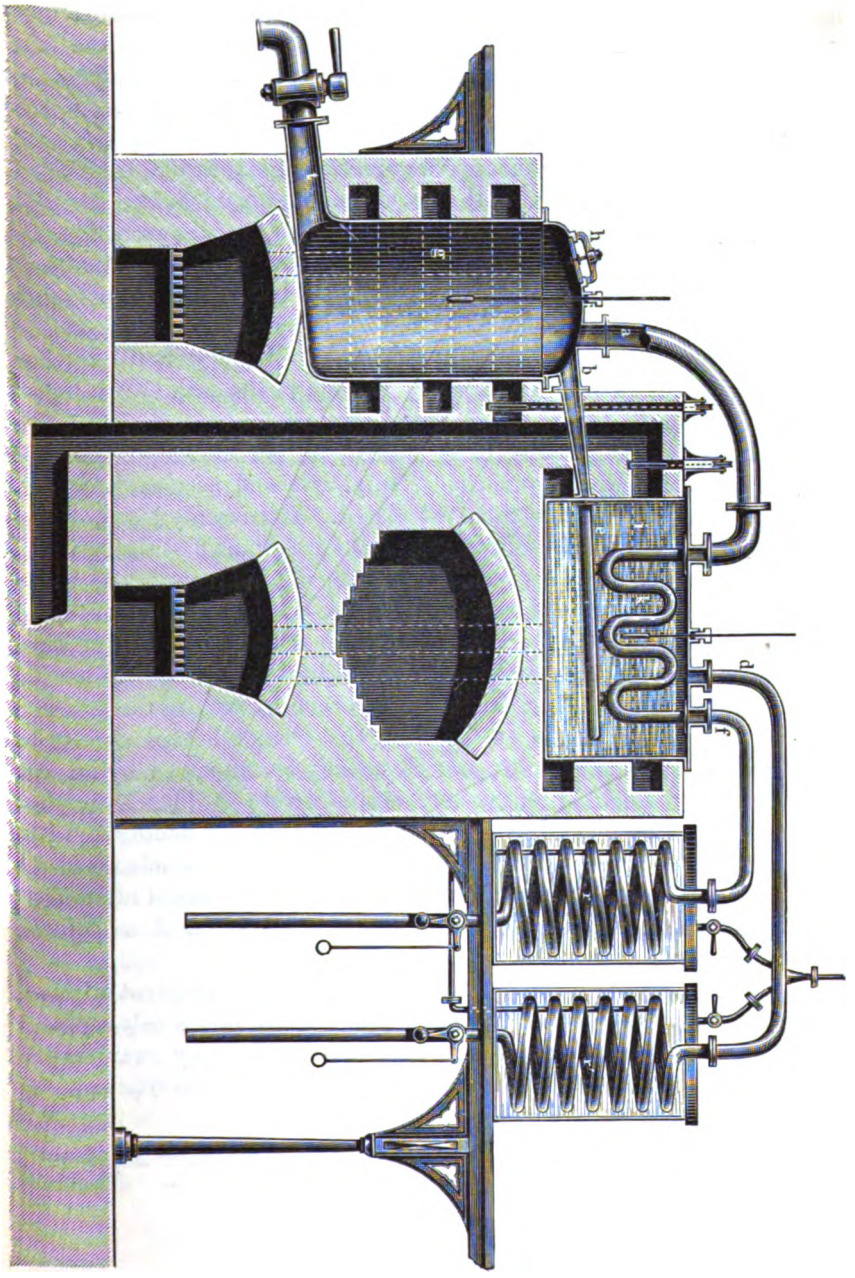
When the still, *g*, is fired, the vapours pass into *k*, and heat the contents of *i* to the boiling-point of phenol. This is hastened by first heating up *i* nearly to that point. The phenol vapour given off in *i* is condensed in the worm *r'*. The vapours passing through the bends of *k* are here separated into a liquid portion, essentially cresol, which collects below in *e* and runs back to *g*, and vapour of pure phenol, which condenses in *r*. When all the phenol has passed over, the cresol, if required, can likewise be obtained pure, *i. e.* free from less volatile products; but in that case *i* must be filled with oil or paraffin, and heated to 201°.

Girard's apparatus could be improved by bending the connecting-pipe *b* so as to make an hydraulic lute, and thus prevent the vapours from passing at once to the back part of *k*. Its action would even then be hardly so perfect as that of the more modern column apparatus, which will be described in the 11th chapter; and it is indeed quite possible (according to private information received from Dr. C. Haüssermann) to use a Savalle still, such as will be described there, for phenol, with a few slight modifications.

It would appear that in crude phenol oils occur which are modified by oxygen and yield brown or red resinous products. Moreover, as we have repeatedly pointed out (pp. 140, 147, 378), rosolic acid is possibly formed, likewise on condition that oxygen be present. This agrees with an observation made by Hager*, according to which white phenol is turned red by traces of ammonia; for the latter yields a red salt with rosolic acid. If really,

* Pharmaceutisches Centralblatt, 1880, p. 77.

Fig. 100.



as Hager assumes, ammonium nitrite is the agent in this case, the nitrous acid will furnish the oxygen. Hence the colouring-matter will be kept out of the finished phenol, if from the first enough oxygen is supplied to complete the oxidation before the pure phenol is distilled. Upon this is based, among others, the process of H. Müller *, who at the same time introduces fractional precipitation (analogous to the fractional saturation mentioned by Behrens, p. 369) of the crude carbolic acid before distillation. The alkaline carbolic liquid contains, besides carbolic acid, some oxidizable bodies which give rise to a brown coloration, and also, especially in concentrated solutions, a considerable quantity of naphthalene and other indifferent substances insoluble in water by themselves. It is diluted with water till further addition ceases to precipitate naphthalene †; the dark brown liquid is exposed to the air in a shallow vessel for several days, with frequent stirring; it is then filtered, its percentage of phenols ascertained, and the quantity of sulphuric acid necessary for precipitating the whole of them calculated. If now only $\frac{1}{6}$ or $\frac{1}{8}$ of the calculated acid is added with frequent stirring, at first the resinous substance, changed by the action of the air, is precipitated, mixed with more or less of the phenols. A further addition of acid precipitates essentially cresol; and after a few trials almost pure phenol, crystallizing after a single distillation, can be obtained by the third and last precipitation. In order to remove the water, a current of dry air is passed over the phenol heated almost to boiling. The aqueous vapour is usually accompanied by an unpleasantly smelling substance, according to Müller a sulpho-compound of phenol, which can be removed by adding a little lead oxide before distilling. (Such sulphur compounds no doubt exist already in the tar; but they may also be formed afterwards by incautious precipitation with strong sulphuric acid, as pointed out p. 376.)

The exposure of the liquor in shallow pans with frequent stirring, recommended by Müller, would no doubt be advantageously replaced by forcing in a finely divided current of air, or by running the liquor down a coke column &c. The same object is attained ‡ by

* Dingler's Journal, clxxix. p. 461.

† This point is not very easily hit; hence it is preferable to employ dilute alkali from the first, as already pointed out.

‡ Stohmann-Kerl's 'Chemie,' vi. p. 1182.

adding ½ or ⅓ per cent. potassium bichromate, and the sulphuric acid necessary for decomposing this, to the crude carbolic acid in the still, and heating gently at first. If this does not suffice to make the phenols distil colourless, more bichromate must be added.

It has been recommended * to treat crude (50-per-cent.) carbolic acid with 1 per cent. of potassium bichromate and the corresponding quantity of strong sulphuric acid in a shallow pan, running in first the acid, then the solution of bichromate, and agitating the mixture for several hours with access of air and in a place exposed to the direct light of the sun. The mixture is allowed to settle, the oil is drawn off and distilled, and the fraction coming over between 170–198° is again submitted to the bichromate treatment, and is redistilled in a still with rectifying column.

According to my experiments it is true that, even on a small scale, from carbolic acid which, in spite of being dehydrated by calcium chloride and properly fractionated, could not be brought to crystallize, a good white crystallizing product was obtained when it was distilled over a little potassium bichromate and the corresponding quantity of sulphuric acid. This product fused at 35°, *i. e.* several degrees above phenol which had been treated exactly in the same way, but leaving out the bichromate and employing only 2 per cent. of concentrated sulphuric acid. No doubt a still higher fusing-point would be attained in operating on a large scale.

By the methods just described it is easy to obtain crystallized phenol, but scarcely in the perfectly pure state—certainly not such as will remain white. The distillation in metal stills must in any case be followed by rectification of the crystallized phenol in glass retorts, or in a copper retort with a porcelain or silver head and an earthenware or silver worm. Base metals must be strictly avoided in this last distillation, because the smallest trace of copper, iron, or lead, &c. colours the product. The condensate is received in glass bottles and is poured into the tin boxes intended for sending out, which are closed except a small opening for inserting a funnel. After standing a few days, crystallization sets in of itself, or is induced by a shock. The mother liquor is now drained off, the box being turned upside down; fresh carbolic acid is then run in, which will crystallize quickly; the mother liquor is drained again; and this is continued till the box is quite filled with crystals, whereupon the opening is closed.

* Wagner-Fischer's Jahresb. 1885, p. 465.

Even in this way carbolic acid remaining white in the air and the light will not always be obtained; sometimes the acid is discoloured even from the first. Hence, before making the last rectification, it should be ascertained that the phenol intended for it does not become discoloured on standing. If it does so, it must be further purified in one of the ways indicated.

According to Ebell * crystallized crude carbolic acid contains substances which are volatile and colourless, but are changed into non-volatile, red or yellowish-brown substances by the action of light, more than by that of heat and air. The substance yielding the red colour passes over principally along with the first, that yielding the yellow colour with the last products of distillation. Neither of them in partial crystallization enters into the crystals of carbolic acid, apart from what is mechanically enclosed in them, but remains in the mother-liquor. They are sparingly soluble in water, but are extracted by water acidulated with sulphuric or phosphoric acid; they are insoluble in benzene. Oxidizing agents, acting during the distillation, change the substance yielding the red colour more than that yielding the yellow colour; oxidizing agents in aqueous solution and in the presence of sulphuric acid destroy them both. The products of oxidation seem to be less soluble in water than the original substances; they are not volatile, or pass over only with the highest boiling fractions. Even the acids distilled from glass vessels often colour very strongly; in such acids no traces of metals could be found.—It is recommended to purify the crude acid by repeated crystallization and subsequent distillation of the crystals. If it is not possible to work up the red mother-liquors, or to sell them at a decent price as "100-per-cent. liquid carbolic acid," it is recommended to treat them with an oxidizing agent in the presence of sulphuric acid, and to follow this up by repeated washings. In less difficult cases it is sufficient to add to the contents of the retort, previous to distillation, a little red oxide of lead with a small admixture of sodium bicarbonate, or some finely pulverized barium peroxide. Mylius † showed that neither zinc oxide nor iron oxide cause the reddening of carbolic acid, but that traces of ammonia or potash do so, and that the reddening is prevented by adding sufficient hydrochloric acid to show a reaction with litmus.

For the following detailed and reliable description of the manufacture of pure carbolic acid, as carried on in Lancashire, I am

* Repert. f. anal. Chemie, 1884, p. 17. † Pharm. Centr. Halle, 1887, p. 72.

indebted to Mr. Watson Smith:—The crude carbolic acid is distilled in cylindrical wrought-iron stills 2 feet 9 inches wide, 2 feet 2½ inches high, with a head 5¾ inches wide, and a thermometer. The worm should be made of zinc—lead, copper, and tin having each been tried and failed. Three different fractions are made: first, water, with some oil; second, good, crystallizable oils; third, oils not crystallizing, containing cresols and naphthalene (compare Lowe's prescription, p. 370). If the crude phenol be good, the second fraction will crystallize on standing. It is well agitated with some highly concentrated and pure sulphuric acid, in the proportion of 1 part acid to 50 parts of phenol by weight; with inferior phenol, 2 parts acid to 50 phenol may be used, but never more: and only one such treatment must be employed; otherwise the oils will not crystallize afterwards. In this process the phenol deepens in colour, turns pink, and becomes perceptibly warm. The mixture, well agitated, is poured *at once* (this is very essential) into the still, and distillation commenced and carried through without stopping and starting again. The first products come over between 150° and 160° C.; and the distillate often crystallizes immediately after dropping. Not much comes over below 175°; and it is better to keep this separate. Usually most comes over between 175° and 185°. At this stage the contents of the retort commence to coke, and the process is stopped. The contents of the receiver are let stand for several hours, to cool completely and crystallize. The mass obtained is set to drain for two or three days, the more thoroughly drained upper portions being from time to time removed. To a portion once crystallized no fresh distillate must ever be run, as it would dissolve some of the crystals again. Care must be taken not to crush the crystals. The oil that drains from them is technically termed "phenylene." This is again distilled and more crystals obtained from it, which are drained; and the resulting "phenylene" is distilled a third time, but without further treatment with sulphuric acid. In distilling the "phenylene oils" it is usual to leave in the retort 1½ gallon (sometimes 2) out of every 20, this residue being technically termed "terebene." It is assumed that the latter contains the oils which would prevent the phenol from crystallizing. When the "phenylene" has thus been exhausted by two or three distillations, it is set aside as "bad phenylene." *

* The expressions "phenylene" and "terebene" are only private marks, and not at all generally used.—G. L.

In lieu of these repeated fractional distillations it has been found advantageous to artificially cool the "phenylene oil" by refrigerating machines. [That actually employed at the works in question is the ether machine (probably Harrison's or Siebe's); but it is well known that much better freezing-machines, *e. g.* Linde's, are in use now.]

All the drained crystals obtained as above mentioned are now fused on a water-bath; the liquid is poured into an iron retort with a zinc worm, and distilled—the first small portion (containing water) being rejected, and most of the remainder received into bottles or other vessels, where it solidifies quickly on cooling, forming a white crystalline mass which is sold as "pure commercial carbolic acid." The small quantity left in the retort is classed as "terebene oil." A purer product than the above is obtained by placing the bottles upside down for a day, re-fusing the drained mass on a water-bath, and pouring it into fresh, perfectly clean and dry bottles or other vessels. The liquid now sets perfectly hard and very white, and is termed "finished commercial carbolic acid."

For "finished medical carbolic acid" the first crystals obtained from "phenylene oils" by draining all night are melted into a glass retort, and a little of a mixture of equal parts of sodium bicarbonate and pure litharge or red lead, well mixed and pulverized, is added. A very small quantity suffices; the lead oxides probably act in retaining sulphur compounds. After standing for some time, distil into a clean dry vessel, rejecting the portions first coming over, which contain some moisture. The crystals obtained are fused on a water-bath; and the resulting liquid is poured into clean dry bottles, in which, on cooling, it forms pure white and solid crystallized carbolic acid.

The following description of the manufacture of carbolic acid in England comes from an official, and hence authentic source (Dr. Ballard's Sanitary Report to the Local Government Board for 1878, p. 151). Carbolic and cresylic acids are prepared from the crude acids by a series of fractional distillations and crystallizations. For these distillations iron stills, capable of dealing with charges varying from 150 to 500 gallons, are used; they are heated by a fire beneath. The crude acid is transferred from the casks in which it arrives at the works to a closed tank, preferably sunk in the ground, from which it is pumped into the still. The residue of the first distillation, which is or ought to be conducted to dryness, is a light and spongy coke, which, when the still is cool, is

broken up with an iron bar and removed through the man-hole. It is used as fuel. During the last part of this first distillation offensive uncondensable gases are given off. When, on subsequent distillation, an acid is distilled off which solidifies at a higher temperature than that which results from the first distillation, the acid is apt to solidify in the pipe, and hence the pipe leading to the condenser is provided in its course with a short-necked opening, capable of closure, through which, if necessary, hot water may be introduced to clear the pipe. The products of condensation are collected in numerous small fractions, and are usually received in a series of galvanized iron vessels, which are left open during the process of their filtering, but covered with a lid when they have become full. Carbolic acid is most abundant in the earlier, and cresylic acid in the later, fractions. The vessels containing the products of distillation are then set aside to cool, when the carbolic acid crystallizes, while the cresylic acid, holding some carbolic in solution, remains liquid. The liquid matter is then drained off through an opening near the bottom of the vessel, and is subjected to a second distillation for the purpose of obtaining the carbolic acid it contains. When all the liquid has been drained off from the crystals, or removed by the aid of a centrifugal machine, the carbolic acid obtained is again distilled, and the cresylic acid, after crystallization of the carbolic acid in the receiving vessels, is drained off by inverting the latter over a trough. By the first distillation and crystallization, as conducted at Lowe's works, a carbolic acid fusing at 29°·5 C. is obtained. The second distillation and crystallization gives an acid fusing at 35° C. The acids, of the fusing-points mentioned above, are next melted in a steam-jacketed vessel and mixed with water; the liquid hydrate of cresylic acid is separated mechanically in the usual manner; and the solid crystalline hydrate of carbolic acid is submitted to fractional distillation, by which process the fusing-point of the dry acid is raised to 42°·2 C. All these are "commercial" acids, and for medical purposes still require refining, in order to remove from them the last traces of neutral hydrocarbons, of the offensive sulphuretted compounds, tar-bases, &c. At Calvert and Co.'s works the commercial acids are refined by suitable acid treatment for the removal of the bases and neutral hydrocarbons, and by treatment with acetate of lead for the removal of sulphuretted hydrogen. After this the acid is re-distilled in glass retorts heated by a sand-bath, each retort taking a charge of about 40 lb., of which four-fifths

are distilled off. The residue in the retorts is a blackish, treacly substance which crystallizes imperfectly, and which is dealt with elsewhere for the recovery of such carbolic acid as it contains. The liquid cresylic acid which results from earlier operations is refined in a similar manner by distillation with acetate of lead; but an iron still is used for this process, and the distillation is carried to the production of a coke.

In order to prevent the nuisance arising from the escape of offensive uncondensable gases, which are sometimes perceptible for a distance of at least 100 yards, the following arrangement is carried out at Mr. Lowe's works. The pipe from the worm condenser, at a distance of a few inches from the place where it issues from the tub, divides into two branches, one of which descends and carries off the condensed liquid, a gas-trap being formed by a bend of the pipe. The other branch ascends and conducts any uncondensed gases to a 6-inch main pipe, which runs along the front of the whole range of stills. From this main a pipe conveys the gases to a small worm condenser, and from this to a stoneware bottle which receives all liquid matters condensed here. A pipe proceeding from this bottle is supplied with a steam jet, which aspirates the gases from the main and drives them onwards through water or milk of lime, contained in a cask, whereby sulphuretted hydrogen is arrested; and from this washer a pipe conveys the residual gases into the ash-pit of a fire. Should the gases chance to ignite, the ignition would not proceed further back than the cask.

The open receivers, described above, are a source of nuisance, from the general odour of crude carbolic acid. This may be lessened considerably by receiving the condensed liquids into covered vessels, as shown in figs. 101 and 102. There is a series of deep narrow pans, *a a*, set side by side with intervals of a few inches between them within a wooden case, *b*, filled with brine, which can thus circulate around and between them. All the upper part of the case is closely covered, so that only the tops of the receivers are seen, which are kept covered by wooden covers. The condensed products are conveyed by a pipe *c* having small branch pipes with taps opposite the several receiving pans, which pipes discharge into the pans below their covers. Should any pan become too full, the surplus can be run off from the upper part by a waste-pipe *d*, screwed into the bottom of the pan, into a drain or channel *e* beneath, leading to the liquid-acid tank. The brine which circulates round the pans is cooled by means of a freezing machine.

Fig. 101.

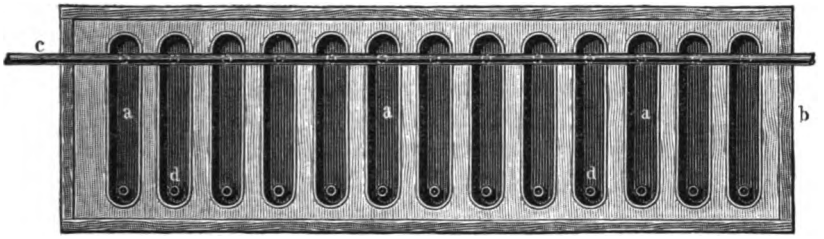
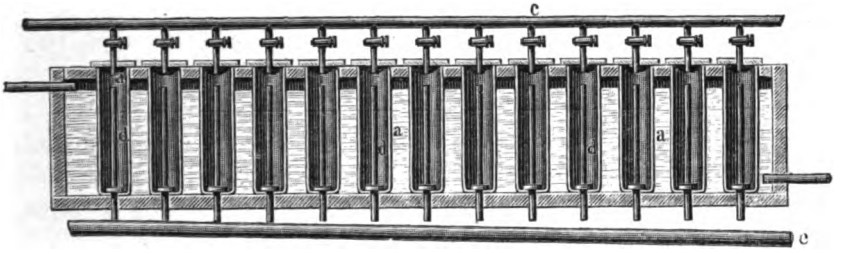


Fig. 102.



The crystallization of the acid thus takes place more speedily and completely; when it is finished, the pans are uncovered, the pipes *d d* are removed, and the liquid portion then runs off into the drain *e*.

The non-crystallizing, higher-boiling portions of the phenols are usually sold as "liquid carbolic acid" or "cresylic acid." The latter can be obtained in a purer state by re-distilling. In doing this, Koehler* once noticed, after about two thirds had passed over as a faintly yellow-coloured oil, that the thermometer suddenly rose from 205° to 300°; thick, white vapours violently issued from the condenser, and the distillate turned as thick as butter. The drawing out of the fire did not stop these phenomena. On opening the still it was found to be half full of a spongy coal. The buttery distillate, after being freed from phenols by caustic soda, entirely resembled the ordinary crude anthracene of tar-distillers, and tested 35 per cent. pure anthracene. This accident, which occurred only once, was probably owing to a local superheating of the still, and proves that anthracene &c. can be formed from the phenols of coal-tar of very much lower boiling-point than its own (comp. K. E. Schulze's theory, pp. 89, 114).

* Ber. d. deutsch. chem. Ges. 1885, p. 859.

The *yield of pure products from crude carbolic acid* is shown in the following table, taken from Kerl-Stohmann's 'Chemie,' vol. vi. p. 1184.

Source of the tar.	Nature of the starting material subjected to the alkaline treatment.	Pure product boiling between 183° and 203°.	Crystallized carbolic acid obtained therefrom.	Liquid carbolic and cresylic acids.
		per cent.	per cent.	per cent.
South Germany.....	Light oil.	34·7	13·1	21·6
Ditto	Creosote oil.	44·8	.....	44·8
Saxony	Light oil.	33·1	13·9	19·2
Saxony, Rhineland, Vienna	?	30·4	6·0	24·4
Sundry	Light oil.	43·7	29·8	13·9
South Germany and Saxony	Light oil.	41·0	28·0	13·0

The considerable loss which takes place in the working-up of crude carbolic acid is caused by its percentage of empyreumatic products, neutral hydrocarbons (especially naphthalene), tar-acids boiling above 203°, and working-losses.

According to Wurtz*, sundry tars contain the following quantities of "phenol" [which probably means all "tar-acids"]:—

Tar from	Wigan cannel coal...	14	per cent.
„	Staffordshire „ ...	9	„
„	Newcastle „ ...	5	„
„	Bog-head	5	„
„	certain kinds of peat	15–20	„

The German tars yield on an average 5 or 6 per cent. of phenols, of which about one third are crystallized carbolic acid.

Watson Smith gives the following analysis (by Lowe's method, p. 394) of crude carbolic acid from Manchester and Blackburn tar, both made from Wigan cannel coal:—

	Blackburn.	Manchester.	Manchester.
	per cent.	per cent.	per cent.
Water (per cent. by volume)	12	13	15
First oil, boiling up to 185° (to be thrown away).....	11	11	10
Carbolic acid distilling below 190°.....	48	45	45
„ „ „ 195–196°...	13½	17½	17½
Solidifying-point of these=61½–62½ per cent.	15°	18°	16¾

* Dictionnaire de Chimie, ii. p. 820.

1000 gallons "carbolic oil" from Manchester tar yield about 50 gallons crude carbolic acid, containing about 65 per cent. of crystallizable phenol.

The yield of phenols from gas-tar has been mentioned also in the general statements, p. 260 *et seq.*, and that from blast-furnaces, coke-ovens, &c. on pp. 81 and 82.

Analysis of Carbolic Acid.

Carbolic acid occurs in commerce in different qualities—as crude carbolic acid, often with the indication of a certain percentage of phenol, as crystallized carbolic acid of different degrees of purity, and as liquid carbolic acid. The latter contains mostly the higher homologues, cresol (cresylic acid), phlorol, &c.; but sometimes there is sold, for medical purposes, "liquefied pure carbolic acid" (acidum carbolicum liquefactum), consisting of 90 parts pure phenol and 10 parts water or alcohol.

Testing of Crude Carbolic Acid.

The properties of crude carbolic acid have been mentioned p. 380.

The percentage of phenols in crude carbolic acid can be *approximately* tested by shaking it up in a graduated tube with twice its bulk of 9-per-cent. caustic-soda solution, added gradually. This is the usual process; that of Hager* (employment of an alcoholic solution of potash) is less used. The volume of the neutral oils (which may be at the top or at the bottom) is now read off. The separation of the oily and aqueous layers becomes more accurate if (as first proposed by Hager) a quantity of petroleum spirit is added in equal volume to that of the tar-oil; of course this volume must be deducted. This or any similar test cannot possibly be accurate, because the alkaline solution, especially if it be somewhat concentrated, dissolves indifferent oils and naphthalene. A check upon the reading of the volume of the neutral oils is: saturating, in a graduated tube, a measured portion of the alkaline liquor with hydrochloric acid and reading off the volume of the phenols separated. Beckurts† estimates that the phenols will dissolve about as much water as the water will dissolve phenols, and

* Wagner's Jahresb. 1872, p. 675.

† Arch. der Pharmacie, 1886, vol. xxiv. p. 572.

even prefers, for *crude* carbolic acid, this test to Koppeschaar's (see below).

The following prescription for testing crude carbolic acid has been drawn up by Mr. Charles Lowe, in the first instance as an instruction to those tar-distillers who supply him with their products, and is followed at most English and some continental works. The specific gravity should be between 1·055 and 1·070. One thousand fluid grains (or, say, 200 c. c.) of the oil are distilled in a retort, without any special condensing-apparatus, and the liquid passing over is collected in graduated tubes. Water first distils, and is followed by an oily fluid. When 100 fluid grains of the latter have been collected, the receiver is changed. The volume of the water is then read off. If the oily liquid floats on the water, it contains light tar-oil. It should be heavier than water, in which case it may be regarded as hydrated acid containing about 50 per cent. of real carbolic acid. The next portion of the distillate consists of anhydrous acid; and when it measures 625 grams, the receiver is again changed. The residue in the retort consists wholly of cresylic acid and still higher homologues of carbolic acid. The 625 grains measure of anhydrous carbolic acid contains variable proportions of carbolic and cresylic acids. These may be approximately determined by ascertaining its solidifying-point, which should be between 15°·5 and 24° C. Having ascertained this temperature, a mixture of carbolic and cresylic acids is made in such proportions as to have the same solidifying-point. This must be adjusted by trial, or a number of standard specimens may be prepared*. The exact point of solidification can be observed more exactly if a minute fragment of crystallized carbolic acid be added, to induce the commencement of the change of state; or the sample may be solidified and the liquefying-point noted. As excess of cresylic acid prevents crystallization, it is evident that in some cases a second fractional distillation should be resorted to, the process being arrested when the thermometer rises to 190°.

We may mention in this place Tidy's and Abel's methods (pp. 361 and 363) for estimating the quantity of "tar-acids" in creosote oil.

* Compare (p. 144) the experiments made by Lunge and Zschokke on the fusing-points of mixtures of pure phenol and pure paracresol. Since "cresylic acid" contains all three isomeric cresols, the indications furnished by Lowe's prescription must be of a very rough character.

Dr. Weyl, of Mannheim, tests crude carbolic acid by a caustic-soda solution of sp. gr. 1·263–1·297. Stronger alkali extracts substances whose sodium compounds are insoluble in the mixture of liquids, and are precipitated as a heavy layer between the oil and the sodium-phenate solution. The substances (which have not yet been examined) belong to the heaviest constituents of coal-tar.

According to Watson Smith, cresol retains less water of hydration than phenol; hence a superior quality of crude carbolic acid, containing less cresol, gives off more water than inferior. In the former case up to 16 per cent. of water is found (comp. analysis of crude carbolic acid, p. 392).

O. Bach* estimates water and phenol in one and the same sample of crude carbolic acid. 50 c. c. of the acid to be tested are distilled in a retort until solid hydrocarbons begin to deposit in the condenser. The distillate is received in a wide burette, holding 100 c. c. and graduated in $\frac{1}{5}$ c. c., which has a glass cock fused on to its lower end. In this burette is previously placed a saturated solution of common salt, about 25 c. c. in volume, and its level is read off exactly. If the carbolic acid be free from water, the distilled oil separates clearly from the salt solution; but if it be aqueous, the oil with the water and brine form a kind of emulsion; by agitating, however, the two layers will quickly appear distinct. The increase in volume of the brine directly indicates the quantity of water contained in the crude acid. Before estimating the phenol, the brine is removed by means of the glass cock. The burette is then filled up to the zero mark with a caustic-soda solution of sp. gr. 1·26, and, after closing with a cork, is strongly shaken and allowed to settle. If the burette was quite clean and especially free from grease, the oil will have completely separated after half an hour, and its level can be observed. The difference from the volume formerly noted at once gives the amount of phenols.

Toth† shakes up 20 c. c. crude carbolic acid with 20 c. c. caustic-potash solution of sp. gr. 1·25 to 1·30, allows to stand for half an hour, and dilutes with water up to 250 c. c., whereupon the tarry constituents of the crude acid separate and are removed by filtration. The residue is washed with tepid water till the reaction has ceased to be alkaline; the filtrate and all the washings are collected

* Chemiker Zeitung, 1882, p. 989.

† Fresenius's Zeitschr. vol. xxv. p. 160.

and diluted to 3 litres. 50 c. c. of this solution are taken out, and to this is added 150 c. c. of Koppeschaar's bromine solution (see below) and 5 c. c. of concentrated hydrochloric acid. The mixture is shaken up now and then for 20 minutes, 10 c. c. solution of potassium iodide is added; and, after standing at most 5 minutes, starch solution is added, and the free iodine titrated with sodium thiosulphate, as will be described hereafter.

The *percentage of water* in phenol, according to Vulpius*, can be approximately tested by adding olive-oil. Carbolic acid, free from water or containing but little water, can be mixed with many times its own volume without becoming turbid. The more water it contains, the less oil it will take without becoming turbid. 4 vols. of crude carbolic acid containing not much above 10 per cent. water will give a clear mixture after being well shaken up with 4 parts of olive-oil; a fifth part of oil will cause strong turbidity.

Casthelaz† gives the following notes on the testing of crude and impure (liquid) carbolic acids. "Crude carbolic acid" is a dark-brown or black fluid, containing phenol, cresol, saponifiable oils, non-saponifiable oils, naphthalene, water, and ammonium sulphhydrate. Its percentage in crystallizable phenol is estimated by Lowe's method (comp. above); "crude carbolic 60 per cent." means an acid which by Lowe's test indicates 60 per cent. of real phenol.—"Liquid carbolic 100 per cent., 95 per cent., 50 per cent." (not to be confounded with "liquefied pure carbolic acid," comp. below) mean an article containing the above percentages of cresol, for those acids do not contain more than traces of real (crystallizable) phenol. They have a more or less unpleasant smell, due to sulphuretted hydrogen, ammonium sulphhydrate, or organic bases. These sulphur compounds are easily detected by shaking up with water and adding subacetate of lead, which produces a more or less abundant black precipitate of lead sulphide. The sulphur compounds can be removed from phenol by agitating it with a solution of sodium bisulphite; the latter is changed into thiosulphate (Casthelaz's patent, 1881). The more or less deep colour of liquid carbolic acid depends upon the washings practised with the crude acid before redistillation. The more bases have been left in it, the darker the acid will turn with age.—The liquid carbolic acids at 95 and 90 per cent. contain 5 or 10 per cent. of

* Wagner-Fischer's Jahresb. 1884, p. 494.

† Bull. Soc. Chim. vol. xlii. p. 574.

water; "liquid carbolic acid 50 per cent." is an artificial compound, which appears in the market only in times of scarcity. It ought to contain 50 per cent. cresylic acid and saponifiable oils, 40 per cent. heavy and light, not saponifiable tar-oil, and 10 per cent. water; but recently articles have been sold under the name by English and German manufacturers which did not even contain 30 per cent. saponifiable oils.

Instead of the ordinary soda test, Casthelaz proposes the following tests :—

1st. Shake up 50 c. c. liquid carbolic acid with 50 c. c. of water. The volume of the carbolic acid ought to remain almost the same; if not, it contains alcohol, glycerin, carbolate of soda, &c.

2nd. Shake up 50 c. c. of the liquid carbolic acid with 50 c. c. of sulphuric acid, diluted with 50 per cent. water. Any slight diminution of the volume of carbolic acid corresponds to its percentage of water. If the diminution of volume is considerable, there is probably carbolate of soda present; and the insoluble upper layer indicates the quantity of cresylic acid and other saponifiable products.

3rd. 100 c. c. liquid carbolic acid is mixed with 100 c. c. caustic-soda solution of sp. gr. 1·38, and diluted with water up to one litre. This will separate the non-saponifiable products; the naphthalene floats at the top in the solid state, and can easily be collected and weighed.

4th. 100 c. c. are distilled in a tubulated retort, the thermometer reaching down to within one centimetre ($\frac{3}{8}$ inch) from the bottom. Notice is taken, 1st, of the water coming over before the cresol; 2nd, of the oily produce distilling between 182° and 190°, and consisting mainly of phenols; 3rd, of the percentage distilling between 190° and 205°, = cresol; 4th, of the residue remaining in the retort.

The test of the *German Pharmacopœia* for "90 per cent. crude carbolic acid" is as follows :—Shake 9 vols. of caustic-soda liquor of sp. gr. 1·079 to 1·08 very thoroughly with 1 vol. of crude phenol and allow to settle perfectly; the portion remaining insoluble, which floats on the top and which is liquid or semiliquid, ought not to exceed 10 per cent. by volume. The product re-precipitated from the alkaline solution by adding hydrochloric acid, in the case of a good article (not containing an excess of cresol), ought to be soluble in at most 30 parts of water.

Hager tests crude phenol of no less than 85 per cent. by shaking

10 c. c. with 20 c. c. glycerin, heating gently, shaking again, and allowing to settle for 6 to 10 hours. The lower, lighter layer is a solution of the phenols in glycerin; the upper, darker one, consists of the impurities.

Analysis of Pure Carbolic Acid.

The properties of chemically pure phenol have been described p. 137. Ordinary commercial "pure" carbolic acid may contain traces of fixed substances—compounds of sodium, calcium, copper, lead, &c., but never more than in most minute quantity. More usually there are present small quantities of higher-boiling phenols, of substances which cause the development of a red or yellowish-brown colour (pp. 140, 147, 378, 386), and of water. Crystallized phenol may contain as much as 5 per cent. water; only when containing 7 per cent. and upwards of water, carbolic acid remains liquid at ordinary temperatures. Water lowers the fusing-point of phenol, but it increases its solubility (perhaps the statements of Allen, ascribing to phenol a greater solubility than that found by all other observers, p. 139, may be explained in this manner). Even 1 per cent. of water may be recognized by shaking the phenol with its own volume of chloroform or ether, which in that case will produce a milky liquid. The quantity of water can be approximately tested by the increase in volume of a concentrated solution of sodium chloride or calcium chloride, as has been described above in connection with the testing of crude carbolic acid. The quantitative estimation of the water can be exactly performed by mixing the phenol with about 5 times its weight of finely levigated lead oxide, and drying at 70° or 80° till the weight is constant.

The higher-boiling phenols greatly lower the fusing-point of carbolic acid. This is most clearly proved by the experiments of Lunge and Zschokke (comp. p. 144), which prove such a lowering of the fusing-point, even when the second phenol is paracresol, whose fusing-point is as high as 32°·5. But since commercial carbolic acid contains even larger proportions of metacresol, which is liquid far below the ordinary temperature, the lowering of the fusing-point is far more considerable than would be indicated by those experiments. The reddish or brownish liquid collecting in the vessels where not absolutely pure phenol is kept mostly contains those higher phenols. Carbolic acid, free from these, even

when containing several per cent. of water, after heating for some time in an open dish and cooling down in a desiccator over concentrated sulphuric acid, solidified to a white crystalline mass, with a melting-point of about 40°; but if it contains a little cresol &c., the residue is brown, and has a much lower melting-point, sometimes remaining liquid. It is most probably these very substances which cause the reddening of phenol by an oxidizing process (pp. 140, 147). They are also indicated by agitating phenol with three times its bulk of pure concentrated sulphuric acid, to which they impart a yellow, brown, or pink colour; also by forming a muddy mixture with glycerin, and by furnishing with bromine a product distinct from pure tribromophenol by not being crystalline, by being coloured, and by fusing below 90°. (Compare also Allen's table of the differences in the behaviour of carbolic and cresylic acids, p. 143.)

Crystallized carbolic acid ought in no case to contain any sulphur compounds which impart to it a nauseous smell, and which can be detected by the subacetate of lead (p. 396), or by boiling an alcoholic solution of the sample with lead hydroxide.

Liquefied pure carbolic acid—that is, pure phenol purposely liquefied by the addition of 10 per cent. water, alcohol, or glycerin—can be distinguished from that "liquid carbolic acid" which essentially consists of cresols &c. (p. 396), by its boiling point (beginning at or below 100°, but quickly rising to 185–190°, whilst the second mentioned article boils at 185–200°), by its solubility in water (the liquefied pure acid requires *at most* 18 parts of water to form a clear solution, while cresylic acid is not completely dissolved even by 50 parts of water), by the different properties of the bromine precipitates, and by all the other distinctive reagents mentioned p. 143. Its percentage of pure phenol is determined by one of the methods described below.

Schlickum* founds a method on the increase of volume produced in liquefied carbolic acid by shaking with its own volume of water. This method is accurate, but the measurement must be made very correctly, as a difference of 1 c. c. is = 8 to 10 per cent. of water.

Vulpius proposed another somewhat similar method, which has been worked out in detail by Salzer†. He also points out that,

* Pharmac. Zeitung, 1884, p. 794.

† Ibid. 1886, No. 1.

whilst anhydrous phenol gives a clear mixture with carbon disulphide, aqueous phenol yields a milky liquid, which requires all the more acid to clear it the more water the phenol contains (comp. p. 396).

Small quantities of cresol are not indicated by these methods; compare Beckurts (Arch. d. Pharm. (3) vol. xxiv. p. 580).

The exact *quantitative estimation of phenol* is always made by precipitating it with bromine as tribromphenol, a reaction discovered in 1871 by Landolt. Tribromphenol forms white star-shaped groups of needles, of a peculiar smell, fusing at 95°, insoluble in water, acids, or somewhat dilute alcohol, but soluble in alkalis, ether, or absolute alcohol. Hence it is necessary to acidify the phenol or its solution in water or dilute alcohol, and to add bromine-water till the liquid has assumed a permanent yellow colour. It is best to heat the liquid till the precipitate fuses to an oil and then to cool it; the precipitate thus solidifies to a cake, which is easily washed, dried, and weighed. If much cresol is present (which also gives a tribrom-derivative, though a liquid one), the precipitate will be a sticky mass. It is therefore not possible to separate phenol from cresol by this method. 100 parts $C_6H_2Br_3(OH)$ correspond to 28·4 $C_6H_5(OH)$; and the quantity of bromine which indicates 1·000 phenol would indicate 1·106 cresol. As a *gravimetric* method, however, this test is not correct, for Weinreb (Monatshefte für Chemie, 1885, p. 506) has shown that the precipitate is not $C_6H_3Br_3O$, but $C_6H_3Br_3,OBr$; but the additional bromine in titrating sets iodine free from KI, so that Koppeschaar's volumetric method is exact after all. Beckurts (Arch. d. Pharm. 1886, vol. xxiv. p. 561) confirms this.

The gravimetrical estimation of phenol by this method is, moreover, much hampered by the fact that the tribromphenol is rather volatile at 100°. But the formation of that compound can be turned to account for an accurate volumetrical estimation, which was first proposed by Koppeschaar*. We here describe his method, which is still mostly employed. The liquids required are:—

1st, a solution of sodium thiosulphate, exactly corresponding to a solution of iodine, containing 5 gr. I per litre;

2nd, solution of starch;

3rd, bromine-water of such concentration that 50 c. c., after

* Zeitschr. f. analyt. Chemie, 1876, p. 233.

being decomposed with potassium iodide, require 18 to 20 c. c. of the thiosulphate solution;

4th, a solution of potassium iodide, containing 125 grammes per litre.

Dissolve 4 grms. of the sample of carbolic acid in water, and dilute up to 1 litre. Put 25 c. c. of this solution into a stoppered half-litre flask, fill it quickly up to the mark with bromine-water, close it, and agitate for some time. Before adding the bromine-water, run 50 c. c. of the same into a small beaker, containing 5 c. c. of the potassium-iodide solution. After standing for half an hour, empty the contents of the half-litre flask into a large beaker, already containing 5 c. c. of the potassium-iodide solution, and rinse the flask twice into the same beaker. Then titrate the liquids, both in the small and the large beaker, with the thiosulphate solution, adding some of the starch-solution, but only towards the end of the operation, and read off, when the blue colour ceases to return after a few minutes.—We have thus employed 25 c. c. of the phenol solution, corresponding to 0·1 gramme of the sample; we have added 475 c. c. bromine-water, and we have standardized 50 c. c. of the latter with a thiosulphate solution of the strength formerly indicated. If we call a the c. c. of thiosulphate required for the 50 c. c. of bromine-water, and b the c. c. of thiosulphate required for the excess of bromine in the 25 c. c. of the solution, the formula

$$(9{\cdot}5\,a - b)\ 0{\cdot}61753$$

directly indicates the percentage of phenol in the sample.

Koppeschaar also mentions that, instead of bromine-water, a mixture of five molecules of sodium bromide and one molecule of sodium bromate can be employed. This mixture is obtained by adding to a solution of caustic soda an excess of bromine, and evaporating to dryness. The resulting mixture of salts is re-dissolved, and, on adding hydrochloric acid, yields all its bromine in the free state:

$$5\,NaBr + NaBrO_3 + 6\,HCl = 6\,NaCl + 6Br + 3\,H_2O.$$

It is, however, not necessary to evaporate the original mixture to dryness; it is sufficient to boil the solution of bromine in caustic soda for some time. Allen* has proved that a boiled

* Journ. Soc. Chem. Ind. 1884, p. 64.

solution of this kind keeps its standard for a long time. He had himself formerly* proposed employing this solution in lieu of bromine-water, and obtaining its standard by calculation, by employing a standard solution of caustic soda for preparing the mixture; but this very indirect method introduces an element of uncertainty, and seems less trustworthy than Koppeschaar's original method, which is also preferred by Waller†.

It seems the most certain method to standardize the bromine water with pure phenol itself. This has been recommended by Diacosa‡, and is also employed by Allen in his last prescriptions for determining the phenol in carbolic soap (see below). Diacosa runs the aqueous solution of phenol into the bromine-water, and determines the end of the reaction by testing a drop of the clear solution with paper soaked in a solution of starch and potassium iodide. This plan had been first proposed by Degener§. Chandelon‖ uses the same indicator; but he employed the brominated caustic soda in lieu of bromine-water. These direct tests are quite incorrect, owing to the formation of tribromophenol-bromide (p. 400).

Beckurts (comp. above) proposes the following as the most certain mode of testing. The solutions employed are:—

1st. A $\frac{1}{100}$ normal solution of potassium bromide, containing 5·939 grm. KBr per litre.

2nd. A $\frac{1}{300}$ normal solution of potassium bromate, containing 1·6666 grm. $KBrO_3$ per litre.

3rd. A solution of 125 grm. potassium iodide per litre.

4th. A $\frac{1}{10}$ normal solution of sodium thiosulphate, containing 12·4 grms. of $Na_2S_2O_3$, 5 aq., per litre, and equal to 0·008 grm. bromine or 0·00156 grm. phenol per cubic centimetre.

Into a well-stoppered bottle put 25 to 30 c. c. of the solution of phenol (1 : 1000), add 50 c. c. each of the solutions of KBr and $KBrO_3$, then 5 c. c. concentrated sulphuric acid and shake vigorously. After ten or fifteen minutes add 10 c. c. of the KI

* Commercial Organic Analysis, 1879, vol. i. p. 307.

† Chemical News, xliii. p. 152. The figures given by Allen for calculating the results, which were repeated in the first edition of the present work, are wrong. Every c. c. of the thiosulphate solution used over and above 6·17 c. c. indicates 0·00157 grm. impurities in 0·1 grm. of the sample, or 1·57 per cent.

‡ Repert. analyt. Chemie, ii. p. 137; Journ. Soc. Chem. Ind. 1882, p. 203.

§ Journ. f. prakt. Chemie, [2] xvii. p. 390.

‖ Bull. Soc. Chim. vol. xxxviii. p. 69.

solution, and titrate the iodine which separates with the thiosulphate solution. This process is accurate whenever solutions of *pure* carbolic acid are to be tested, or mixtures from which such can be isolated, but it fails in the case of crude carbolic acid or other mixtures where cresol is present.

Since the higher-boiling phenols are much less soluble in water than real carbolic acid, or even insoluble, the direct application of Koppeschaar's method, as will be easily understood, yields very unsatisfactory results with creosote oils containing such higher phenols*. In this case the phenols may be dissolved in caustic-soda solution, and this solution may be titrated with bromine-water in the presence of an excess of acid; but in the best case only approximate results can be thus obtained, especially since the calculating factor for the higher-boiling phenol is quite different from that for carbolic acid (see p. 400).

Leube's colorimetric method, with employment of ferric chloride†, and Nietsch's method of converting the phenols into sulphonates of barium or lead and estimating those metals‡, can evidently not yield any accurate results.

Allen§ recommends the following process for *determining phenols in "carbolic soap:"*—Five grams weight of the sample are dissolved in warm water, with addition of from 20 to 30 c. c. of a 10 per cent. solution of caustic soda. The cooled solution is then agitated with ether, and the ethereal layer separated and evaporated at a low temperature. The weight of the residue gives the amount of hydrocarbons, &c. The alkaline liquid separated from the ether is then treated in a capacious separator with an excess of strong brine, which completely precipitates the fatty acids as sodium salts. The liquid is well agitated, and then passed through a filter. In cases where the soap does not readily coagulate, an addition of a small quantity of tallow or palm-oil soap, previously dissolved in water, will usually overcome the difficulty. The precipitated soap is washed twice with strong brine, the washings being filtered and added to the main solution, which is then diluted to one litre. 100 c. c. of this solution (=0·5 gram of the sample of soap) are then placed in a globular separator, and acidu-

* Comp. Kleinert, Zeitschr. f. anal. Chemie, xxiii. p. 1.

† Dingler's Journal, ccii. p. 308.

‡ Wagner's Jahresber. 1879, p. 1036.

§ 'Analyst,' 1886, p. 103.

lated with dilute sulphuric acid, when it should remain perfectly clear. Standard bromine-water is then added from a burette, the stopper of the burette inserted, and the contents of the burette shaken vigorously. More bromine-water is then added in the same way, until the liquid acquires a faint but permanent yellow tint. If crystallized carbolic acid has been employed for making the soap, the bromine derivative is precipitated in snow-white crystalline flocks, which allow the faintest yellow tint due to excess of bromine to be observed with great facility. If cresylic acid be the chief phenol present, as in the case of soaps made with Calvert's "No. 5 Carbolic Acid," the precipitate is milky, and does not separate well from the liquid, but the end of the reaction can still be observed. The addition of a solution containing a known amount of crystallized phenol is a useful device in many cases, as the precipitate then curdles readily, and the yellow coloration can be easily seen.

The bromine solution is made by mixing one measure of saturated bromine-water with two measures of water. This solution is approximately of 1 per cent. strength, and should be run out of a closely-covered Mohr's burette [no doubt a burette with glass tap would be preferable]. The last few c. c. of the solution contained in the burette should never be employed. The bromine-water must be standardized immediately before or after use by a solution of Calvert's No. 2 or No. 5 carbolic acid, according to the kind of acid the titration has indicated to be present in the soap. This solution is made by dissolving 0·5 gram of the phenol in 20 c. c. of a 10-per-cent. solution of caustic soda, together with 5 grams of a non-carbolic soap. The solution is then precipitated with brine in the same manner as the sample, the filtrate diluted to 1 litre, and 100 c. c. acidulated and titrated with the bromine solution used for the sample. The volume of bromine solution used is that required by 0·050 gramme of coal-tar acid of approximately the same quality as that contained in the soap.

The remaining portion of the liquid filtered from the precipitate of soap is best used for isolating the bromo-derivatives. It is acidulated with dilute sulphuric acid, and bromine water added in slight excess. From 5 to 10 c. c. of carbon disulphide is then added, the liquid well agitated, and the carbon disulphide tapped off into a small beaker. The aqueous liquid is agitated with fresh quantities of CS_2 (of 5 c. c. each), till it no longer acquires a red

or yellow colour. The carbon disulphide is then allowed to evaporate spontaneously, when a residue is obtained, consisting of the brominated derivatives of the phenols present in the soap. If crystallized carbolic acid of fairly good quality was introduced into the soap, the bromo-derivative is obtained in fine long needles having very little colour; and if all heating was avoided during the evaporation of the CS_2, the weight of the residue multiplied by 0·281 gives a fair approximation to the amount of carbolic acid. But if a crude liquid article has been employed, consisting mainly of cresol (cresylic acid), *e. g.* Calvert's "No. 5 carbolic acid," the bromo-derivative will be deep yellow, orange, or red, with little or no tendency to crystallize, and the weight will not afford even a rough indication of the amount of coal-tar acid present.

By testing in this way, Allen found great deviations from the quantities of carbolic acid stated to be present by the manufacturers, *e. g.* only 3·6 and 3·7 per cent. of phenol in "Carbolic Toilet Soap, ten per cent."

Applications of Carbolic Acid.

In the pure state phenol is employed in the manufacture of artificial colours, especially of picric acid and corallin; these are not very much used as colours now, but picric acid and its salts are coming into extensive use for the manufacture of explosives, one of which is "melinite." Also some azo-colours have been made with it; and undoubtedly many other applications of it and its homologues will follow in this line. But it is very doubtful whether it will ever pay to employ phenol as a starting-point for preparing rosaniline, as has been proposed. Phenol is also the starting-point for the manufacture of salicylic acid.

Most of the carbolic acid is used for antiseptic purposes. For disinfecting sewers, stables (in the case of cattle-diseases), or even human dwellings, the cheaper descriptions, which are liquid and contain cresol, are probably as valuable as crystallized phenol, and also for preserving hides, bones, &c. for sea carriage. The preservation of wood by pickling with cresote oil is founded, at least partially, on the same principle. The preservation of meat in the same way has often been proposed, but does not appear to be practicable, owing to the very tenaciously retained smell and taste

of carbolic acid. The latter has also been proposed for preserving beet-root juice*.

Harcke (G. P. 16022 and 19633) adds carbolic acid in the currying process to the usual mixture of alum and salt; he also makes "artificial leather" by treating fabrics with a solution of glue and thereupon with a mixed solution of alum, salt, and carbolic acid.

For medical purposes, especially for internal use, as well as for Lister's antiseptic treatment of wounds, and for cleaning the instruments, hands, and clothes, the purest crystallized acid is always preferred, both on account of its higher solubility and of its less unpleasant smell, which can be entirely masked by a little oil of geranium†. Touching its solubility, some phenols of lower melting-point are more soluble than others of higher melting-point—evidently because the lowering of the melting-point is caused more by the presence of water than of cresol. The usual requirement is that 1 part of phenol should give a clear solution with 19 parts of water.

Crude sodium carbolate is employed as a protection against dry-rot, under the name of "house-preservatory."

Carbolic-Acid Preparations.

These are mostly mixtures of crude carbolic acid with lime, frequently of but little value as disinfectants. We shall enumerate only a few of them.

Macdougal's Disinfecting Powder is a mixture of crude carbolic acid with impure calcium sulphite (made by passing sulphur dioxide over heated limestone).

Calvert's Carbolic-acid Powder is a mixture of carbolic acid with the siliceous residue from treating china-clay with sulphuric acid (in the manufacture of patent alum). It ought to contain from 12 to 15 per cent. of carbolic acid; but the percentage is often far below this; it is ascertained by distilling, say, 100 grams in a glass retort. The distillate is partly oily, partly aqueous. The oily portion ought at least to be tested with caustic-soda solution (p. 143), since it generally contains valueless indifferent tar-oils. The phenol contained in the aqueous portion can be estimated by

* Cunisset, Bull. Soc. Chim. 1874, xxi. p. 47.

† Compare what is said on the solubility and other properties of pure phenol in Chapter III. (p. 139 *et seq.*).

bromine-water. Disinfectants containing lime should be slightly acidified before distillation.

Recently Messrs. C. Calvert & Co. have manufactured also a 50-per-cent. preparation in tablets *.

Süvern's Disinfecting Mass† consists of lime, magnesium chloride, and tar, and only indirectly belongs to this class.

Carbolic-acid Soap is generally sold as containing 10 per cent. or even 20 per cent. of carbolic acid, but very often contains much less (comp. Allen's analyses, p. 405), and in any case loses some of it in the course of time by evaporation. The cheaper descriptions contain mostly cresol.

Holtz's Phenolith ‡ is made by dissolving anhydrous boric acid in phenol or cresol, which take up about 40 per cent.; the mass forms a stiff paste, and can be converted into a powder by adding a little common salt, borax, or saltpetre.

Phenol-zinc solution is employed by Busse § for preserving the timber in the cellars of breweries, distilleries, &c. from decay and dry-rot; also hop-poles, vine-stakes, &c. The solution is laid on with a brush, preferably after being mixed with magnesia. [Evidently this treatment will be dearer and not so efficient as creosoting under pressure, p. 343 *et seq.*]

Naphthalene.

Naphthalene is one of the most abundant constituents of coal-tar. Its proportion is rarely below 5 per cent., and it may amount to perhaps 10 per cent. of the weight of the tar. Large quantities of it are obtained in the crude state, mostly unintentionally, by the cooling down of creosote oil; the first portions of this sometimes solidify almost entirely. This crude naphthalene was formerly considered a nuisance, as the buyers of creosote oil objected to it, and there was no outlet for it. Even now nothing like the whole of the naphthalene contained in coal-tar can be utilized otherwise than as an admixture to creosote oil, or as fuel; but there is already a pretty considerable demand for colour-making and for carburetting gas (see end of this chapter), and a good deal of naphthalene is therefore now taken out of the creosote oil for this purpose.

* Chem. News, xl. p. 38.

† Compare Schrader and Berens, Wagner's Jahresb. 1871, p. 702.

‡ German patent, No. 6498.

§ Chemiker Zeitung, 1885, p. 602.

Livesey and Kidd (U. S. P. 258778) propose doing this more efficiently by heating "dead oil" in a closed boiler, and passing a current of air over the surface of the liquid. The air carries off the naphthalene and a little oil, which are condensed in a chamber. The condensed mass is immediately utilized for the manufacture of an article suitable for carburetting air or gas, by reheating it and casting it in cold-water jacketed moulds, like candle-moulds, but wider at the top. The sticks are taken out of the moulds the moment they are set, and the oil (which is all on the surface) is wiped off before it can sink into the naphthalene. Without the water-jacket, the oil would not separate.

This process can at the best only yield a very badly refined sort of naphthalene. In Europe, at any rate, only such naphthalene is now saleable which does not readily turn pink on exposure to the air; and this can only be made by more careful treatment, including hot-pressing, chemical washing, and distilling.

The *hot-pressing* of crude naphthalene is perhaps the most important process for refining it; some even assert that it can be so conducted as to dispense with chemical washing before distilling the naphthalene. This process is carried out in presses with hollow plates heated by steam, like stearin presses, or the presses used in the refining of anthracene (comp. p. 300). Of course very much depends upon properly regulating the temperature. The higher this is kept, the more complete will be the removal of the impurities; but then a good deal of the naphthalene itself will be removed as well, long before its own melting-point is attained, as its solubility in the accompanying oils increases rapidly with a higher temperature.

The operation of separating the naphthalene from the impurities may also be carried out by heating the impure mass to a certain temperature, and then subjecting it to pressing or centrifugal action; but this is less efficient than the treatment in a steam-heated press (comp. anthracene, p. 300).

The processes for refining naphthalene have now been improved so far that a perfectly pure article can be made at a comparatively very low cost from the crude naphthalene crystallizing out of creosote oil, and some workmen even prefer this to the naphthalene from carbolic acid; but at other tar-works pure naphthalene is exclusively made from the just-mentioned source.

This naphthalene is made from the same oil that serves for

preparing phenol, viz. from the residual oil remaining after the alkaline treatment. This is decidedly rational, as thus one of the expensive purifying agents has been applied beforehand to another purpose. Indeed, when the oils drawn off from sodium carbolate (p. 374) are distilled in the light-oil still (see next chapter), at first a little light oil passes over, but afterwards almost pure naphthalene. This is seen on mixing a sample of the distillate with cold water, when no more oil collects on the top, but white crystallized masses float all over the water. The receiver is now changed, and the distillation is continued with the precautions to be described below for preventing any choking-up. The receiver contains a white crystallized magma, from which, after cooling, the naphthalene is separated by pressing. This ought to be done in a *hot* press.

This first distillation is often omitted, and the naphthalene obtained from the oils in question by simply allowing the liquid to cool; but then much less is got, a good deal remaining dissolved in the liquid portion.

Usually the pressed naphthalene (which, in spite of the oils being removed, quickly reddens in the air) is chemically washed. This is more easily effected if the naphthalene be treated soon after pressing, before the adhering oils have been changed by the air. The colour may arise from the formation of rosolic acid from adhering traces of phenol (p. 386), or from oxidation of empyreumatic resins ("Brandharze"). When once the oils are removed, it is all the better if the air thoroughly acts upon the naphthalene and colours it *before* the chemical washing and distillation.

The washings, if the oils have not been previously submitted to an alkaline treatment, must begin with this. The caustic liquor may be of any convenient strength. The treatment is effected in closed iron vessels, heated above the fusing-point of naphthalene (79°) by a steam-jacket or a coil, and preferably provided with a mechanical agitator. With very impure naphthalene this treatment should be repeated. In any case the fused naphthalene must be mixed up for some time with the liquor; and after the latter (which collects at the bottom) has been run off, the naphthalene must be washed with hot water, which will now rise to the top.

With better crude naphthalene, especially that distilled in the manner mentioned above from carbolic-oil residues, the alkaline treatment may be dispensed with, and the washing begun with

sulphuric acid, which in the concentrated state removes the residual phenols in the shape of sulphonic acids. Vohl* recommends sulphuric acid of 45° Baumé (=sp. gr. 1·453). According to my experience this is too weak; acid of at least 1·700 sp. gr. should be employed. The strongest vitriol, of sp. gr. 1·84, is even better; but at that temperature it dissolves much naphthalene; so that less, though of a better kind, is obtained. At some works they wash first with dilute, and then with strong sulphuric acid. On the large scale 5 to 10 per cent. of acid will suffice.

The mixture with sulphuric acid takes place in wooden or iron vessels lined with lead, heated by indirect steam and provided with an agitator: the subliming of naphthalene during this operation is a little troublesome. Now follows washing several times with water and then with weak alkaline liquor, to remove all acid, and finally distillation (see below).

The washing of naphthalene, both with acid and alkali, is preferably performed in steam-jacketed vessels, provided with a horizontal agitating shaft.

It is not easy to make naphthalene, even by hot-pressing, chemical washing, and distilling combined, that will keep its colour for any length of time; usually, although sometimes only after the lapse of some months, it turns pink on standing, and thereby becomes difficult to sell. The object of obtaining permanently white naphthalene can, however, be accomplished by the following process, worked out by myself† on the assumption that the pink colour is caused by the formation of rosolic acid or similar compounds from traces of phenols escaping the previous treatment, or at all events from some other oxidation which can be made innocuous by performing it purposely *before* the last distillation, and then removing the product by that last operation. This can be done by melting the naphthalene with sulphuric acid of sp. gr. 1·70 up to 1·84 and adding some oxidizing agent, preferably finely ground manganese ore or artificial manganese dioxide ("Weldon mud"), whereupon the mass is washed and distilled. By this process a product has been obtained, both by myself and others, which has kept its pure-white colour for a number of years; whilst the best samples of commercial "pure" naphthalene, kept in exactly the same place beside the former, have turned

* Journ. f. prakt. Chemie, cii. p. 29.

† Ber. deutsch. chem. Ges. 1881, p. 1755; Chem. News, xliv. pp. 65 & 142.

pink long before. It seems a good plan to melt the naphthalene in a steam-jacketed vessel, to mix it thoroughly with, say, 5 per cent. of ground manganese ore, then to add from 5 to 10 per cent. of sulphuric acid, and continue the agitation for ½ hour or a whole hour. It may also be recommended to add the chemicals in two portions. Where the naphthalene is got from the treatment of carbolic acid, no special alkaline washing need be performed; otherwise this should be done before the treatment with manganese and sulphuric acid.

In any case a washing with water must follow both the alkaline and the acid treatment. Of course hot water must be employed; and this can be done very conveniently by running the melted naphthalene into a lower vessel, charged with nearly boiling water, and agitating all the time.

Subliming and Distilling Naphthalene.

The washed naphthalene is always either sublimed or distilled. The *subliming* can be done on a moderate scale in the apparatus fig. 103 (taken from Wurtz). *a* is a pan for melting the naphthalene, heated by the fire on the grate *b*; *c* is the snore-hole; *d d* are flues. The pan is covered by a tub, *f*, hung by chains from a small crane *e*; in its top there is a small air-vent. The naphthalene sublimes into the tub, forms crusts on the sides, and is knocked out at the end, after moving the tub sideways. The fire should not be strong enough to cause the naphthalene to melt in the tub and run back into the pan.

The apparatus fig. 104 is intended for a larger scale of working. *a* is a shallow iron pan, say 10 feet × 7 feet × 3 feet deep. The steam-coil *b* on its bottom serves for heating. The pan is covered by the slanting wooden roof *c*, whose lower part can be turned back into the position shown by the dotted lines. To this is attached a wooden chamber, *d*, say 16 × 10 × 5 feet, with a working-door, *e*, and a flap on the top, serving as safety-valve. The heat of the "dry" steam in the coil *b* suffices for subliming the naphthalene; it should not go so far as to give rise to distillation. The naphthalene collecting in *d* is taken out at intervals of a few days.

Sometimes steam blown into the mass ("wet steam") is preferred to dry steam. In this case there should be a compartment between the pan and the subliming chamber, in which the condensed steam-water and a little melted naphthalene may collect.

Fig. 103.

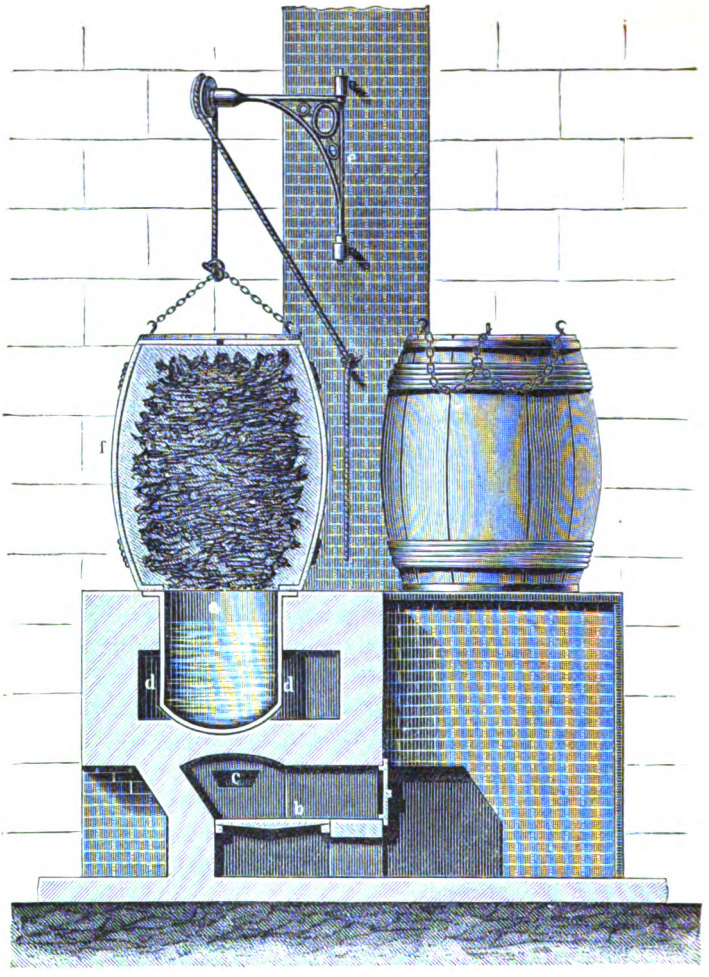
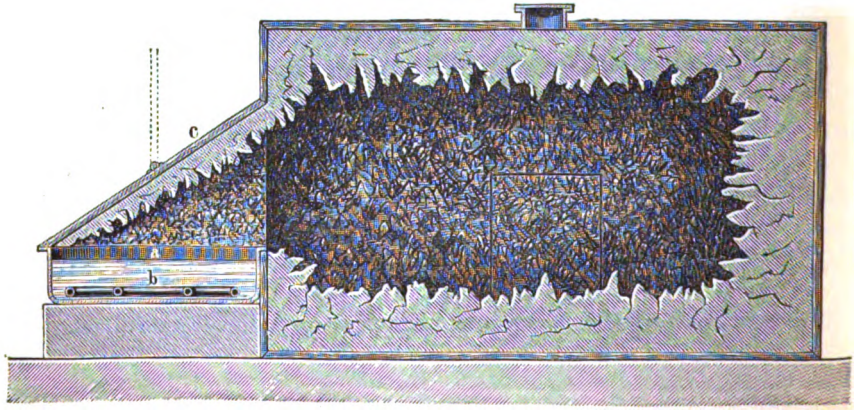


Fig. 104.



Some state that it is better to mix the naphthalene with sand before subliming; but this seems to be quite unnecessary.

Hirsch* proceeds as follows. The sublimation chamber is an isolated structure of masonry, the walls being one foot thick, 17 feet long, 10 feet wide, and 10 feet high, with a light double roof, covered with roofing-felt on the exterior, and having within a plastered ceiling [sheet iron would be preferable]. At one end of the building is a door, resting in a groove in the frame, which during operations is luted with clay. At the other end, without the main wall, there is a cast-iron pan extending the whole width of the building, with a fire-place and flues running round the pan. Two covers, one of which is dome-shaped, are suspended a short distance above the pan and act somewhat in the manner of dephlegmators. The pan communicates with the chamber by an opening in the end wall; and a wooden lid lined with sheet-iron, hinged on the main wall just above the opening, and reaching to the outer edge of the pan, affords a means of filling or emptying this. In the roof there is an iron air-pipe, projecting 4 inches below the ceiling and 18 inches above the roof; a pan suspended just below this serves to collect any condensed water. The operation is carried on as follows:—

The crude naphthalene which has crystallized out from the creosote oils is allowed to drain for two or three days, is mixed with 3 or 4 per cent. of slaked lime, and is charged into the pan. After the sublimation has gone on for some time, samples are taken out of the pan at intervals, and when it is observed, by the non-crystallization of a sample on cooling, that the naphthalene has been expelled, the pan is emptied and charged again. The once sublimed naphthalene is melted in a cast-iron pan provided with an exit pipe; and is here washed first with 20 per cent. caustic-soda liquor, then with 6 per cent. sulphuric acid of sp. gr. 1·84, with which it is agitated for 15 or 30 minutes, and at last washed with water. It is then once more subjected to sublimation until 80 per cent. has been collected. [This process, apart from being evidently carried out at a small works, without mechanical washers &c., suffers from the necessity of twice subliming, and will for all that hardly yield *permanently* white naphthalene.]

It has also been attempted to effect the sublimation by blowing in hot air by means of a fan-blast; but this has been given up

* Chemiker Zeitung, 1884, p. 839.

again. Ordinary air easily produces a fire; and a previous removal of the oxygen by live coals is too expensive. Moreover the condensation is more difficult than when the heating is produced by indirect steam.

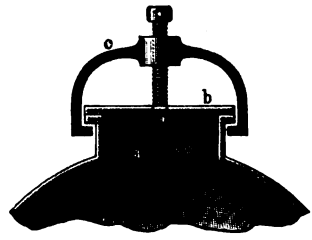
Much preferable to sublimation is the *distillation* of naphthalene, both because it permits larger quantities to be dealt with and because fractionation is in this case much more easily effected. It would appear that all the factories that turn out the best naphthalene distil it. The stills are shallow wrought-iron vessels, holding a ton or upwards, heated by a direct fire, but protected against its first action by a curtain arch; they are provided with a man-hole, a safety-valve, and a very high head (up to 7 feet), which can be furnished with contrivances for dephlegmation, but which already acts in this direction by the cooling effect of the air.

The condensation is effected either by a simple iron worm similar to those used for tar—but with the water in the tub always kept at 80° at least, and sharp elbows and the like (where at the end of the operation solid naphthalene might accumulate and cause in the next operation a dangerous tension in the still, or ultimately an explosion) being avoided. If after all a plug of naphthalene should choke up the worm without its presence being noticed at once (in which case it could be melted by boiling water), the safety-valve will blow out. This is a signal for instantly drawing the fire; in the worst case the still must be cooled from above by pouring water upon it.

All danger of choking-up is avoided, when distilling in a vacuum, by employing an air-tight receiver and exhausting the air by means of a pump; and we would greatly recommend this way of distilling naphthalene for other reasons as well.

In lieu of an ordinary safety-valve (which easily gets fast and anyhow might not act quickly enough) a contrivance like that shown in fig. 105 may be advantageously employed. Upon the still is fixed a flanged pipe, *a*, 12 inches wide, covered by a metal plate, *b*. Hemp packing and the weight of *b* suffice for keeping the joint tight without screwing down the arm *c*. The latter is quite loose; and its only object is to prevent the cover *b* from being violently

Fig. 105.

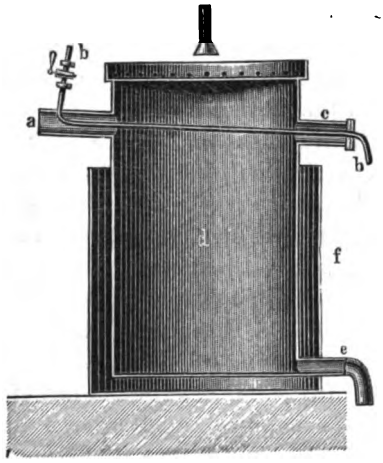


jerked away whenever it is lifted by excessive tension in the still. *b* will then be lifted as far as *c* allows it, and will permit the vapours to escape.

Watson Smith (Journ. Soc. Chem. Ind. 1882, p. 343) thinks it safer and simpler to have a small hole bored in the still-top and closed by a cork, which, if there is too much pressure, would be blown out with some force. For large stills the outlet thus gained for the vapours would be hardly sufficient. Compare also what has been said in the case of tar-stills, pp. 212 and 232.

Some manufacturers, in order to avoid any danger of choking up, work without a worm, with an apparatus like that shown in fig. 106. The vapours pass through the tube *a*, kept warm by the

Fig. 106.



steam-pipe *b b*, into the wrought-iron cylinder *d*. Opposite *a*, running in the same slanting direction, is a pipe, *c*, through which the steam-pipe *b* comes out. Thus *a* is prevented from being choked up; and *c* also serves for an occasional cleaning-out. *d* is placed to two thirds of its height in a wider cylinder, *f*. If the cooling effected by the outer air is not sufficient, water is run upon *d*, which collects in the outer cylinder and runs away. But the temperature in *d* is kept high enough for the naphthalene to remain liquid and to run out through the pipe *e*. It is collected in shallow iron dishes, where it solidifies into cakes, which are either broken up and packed at once, or once more subjected to hydraulic pressure.

In distilling, first of all a little water and light oil appears. When the thermometer (in the vapour) has risen to 210°, the receiver is changed and pure naphthalene collected up to 230°, or even 235°. Then either the still is stopped and the residue run to the creosote oil, or the distillation is continued into another receiver, and the impure naphthalene collecting there is again purified. Apart from the danger of choking up, the distillation is easy and quick.

G. Link (G. P. 35168) presses crude naphthalene repeatedly in hydraulic presses, distils it, and treats the distillate in a cast-iron agitator, similar to those used for manufacturing nitrobenzol, with a solution of soap at about 85°. Most of the mass enters into solution; the mixture is run into wooden tanks, is cooled down to 50° by cold water, dehydrated in a centrifugal machine, washed and distilled. The naphthalene now passes over almost chemically pure, as a limpid liquid which solidifies to a large-flaked, snowy-white, crystalline mass. The impurities of crude naphthalene remain dissolved in the mother liquor.

Stenhouse and Grove* heat the, otherwise purified, naphthalene with a small percentage of sulphuric acid to a temperature of 180°, distil the resulting black mass in a current of steam, and repeat this process till the product dissolves at 100° in an excess of concentrated sulphuric acid without any colour. This process, employed by them for scientific purposes, would hardly pay on the large scale; and it would be very troublesome to sublime the naphthalene mixed with acid.

The distilled naphthalene is always run out of the condenser in a liquid form, and is usually run upon a large metal plate or shallow pan, where it solidifies, and is then broken up into small pieces, and sometimes ground into powder. Sometimes special smaller moulds are employed. The naphthalene required for the albocarbon light (see below) is cast into sticks, like those of refined sulphur ("brimstone in rolls"). This is done by means of hardwood moulds, with a little taper to facilitate the getting out, or by a moulding machine such as is used at candle-works.

Where large quantities of pure naphthalene are made, the vapours arising from the liquid naphthalene in the moulds, previous to its solidification, may cause an appreciable nuisance. This is prevented by providing the pan, serving as a mould, with an

* Ber. d. deutsch. chem. Ges. 1876, p. 683.

hydraulic lute, and covering it up by a cover suspended from a crane, so that it can be removed after the naphthalene has cooled down, in order to clear the mould. This apparatus resembles the oxide-of-iron purifiers of gas-works.

Examination of Naphthalene.

The properties of pure naphthalene have been described p. 123. Commercial naphthalene is now-a-days required to be as chemically pure as possible. It ought to volatilize without any residue, to fuse exactly at 79°, to boil at 217–218°. In order to see at once whether a sample of naphthalene will turn pink or not, tests are made with sulphuric and nitric acids. On dissolving the sample in pure hot concentrated sulphuric acid, the latter should only turn faintly purple or pink: I have never yet met with a sample which left the acid entirely colourless, when dissolved in somewhat large quantity. Even the best commercial brands sometimes turn the acid pretty strongly red. The other test is made by pouring pure, *not* fuming, nitric acid on the bottom of an exsiccator and placing the naphthalene in a watch-glass above it, covering up the whole as usual. If the sample remains white for half an hour it is good, and if for two hours it is excellent. Inferior descriptions soon turn pink. After some hours all samples turn yellow, probably owing to the formation of nitronaphthalene.

The presence of phenols in naphthalene is discovered by boiling the sample with a dilute solution of caustic soda, cooling, filtering, and adding to the filtrate bromine-water and hydrochloric acid; any phenols present will now be precipitated as brominated compounds.

Quinoline bases are discovered by dissolving the sample in concentrated sulphuric acid, pouring the solution into water, filtering, making the filtrate alkaline, and distilling, when the quinoline bases will pass over with the aqueous vapour, and will be recognized by their peculiar smell.

C. Häussermann (private communication to the author) points out that even a most thorough washing with acid and alkali does not free the naphthalene from certain other hydrocarbons which do not affect either the boiling-point or the other outward properties of naphthalene, but which make themselves felt in the subsequent manufacture of naphthylamine, naphthol, &c. These

impurities are said to be removable only by certain solvents; but it would appear as if the hot-pressing of the naphthalene crystals, as it is now pursued at most works, equally tends to remove them.

Employment of Naphthalene.

The naphthalene occurring in such large quantities in coal-tar (usually from 5 to 10 per cent., sometimes perhaps in excess of that*) was formerly one of the least welcome of its constituents. It generally accumulated in the creosote oil and caused inconvenience by crystallizing there; sometimes it led to the rejection of creosote oil for pickling timber (p. 349). In such cases nothing remained but to work it into the pitch, or burn it for soot, or to employ it as fuel, mixed with coal. Even now crude naphthalene is sometimes employed as fuel in the melted state, for instance for heating the tar-stills. In that case the liquid naphthalene is injected into the fire-place by means of a steam-jet exactly like tar or tar-oils (p. 168 *et seq.*).

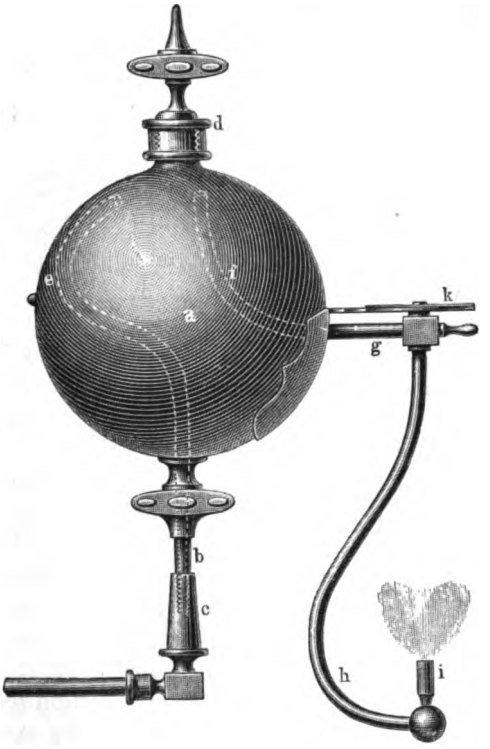
The applications of naphthalene for the *manufacture of artificial colours* were formerly very scanty, in spite of a great many efforts in this direction; dinitronaphthol (Manchester yellow) and naphthalene red (Magdala red) were for a long time the only colours made from naphthalene. When the series of phthaleine colours (eosine &c.) was discovered, in 1876, a demand for phthalic acid sprang up, for which naphthalene is the starting-point. But far more important in this respect was the discovery of the long series of azo-colours, nearly all of which date from 1878. For most of these naphthols, especially $\beta C_{10}H_7(OH)$, are required, and for the preparation of these the purest naphthalene is demanded. The manufacture of naphthol colours in Germany alone now amounts to at least a ton per day.

One of the most important uses of naphthalene is at present that for *carburetting gas*. This has been frequently proposed, *e.g.* by Bowditch (B. P. 2937, 1862); but the principal impetus to this industry was given by the inventions of Livesey and Kidd, latterly associated with H. Vale, of Hamburg (G. P. 2075,

* Exceptionally coal-tar is found containing hardly any naphthalene. Such has been the case with the Manchester Corporation Gas-works tar in 1873 and 1874, according to Watson Smith. He found naphthalene in cannel-coal tar, along with paraffin. On the other hand, Crace Calvert states the percentage of Newcastle tar=58 per cent. naphthalene, which is simply absurd.

8644, 9840, 19012, 32255). Their apparatus, called the "*albo-carbon light*," has been attracting much attention. It is principally adapted for small flames, and is stated to save more than half the gas consumed for the same illuminating-power in the best argand burners; so that it is very economical, in spite of the cost of the naphthalene. It is a drawback that, if the apparatus is allowed to get too hot, there is too much volatilization of naphthalene and the flame burns smoky; if it were still further neglected, the naphthalene would boil and the apparatus would burst.

Fig. 107.



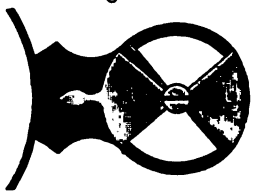
In experiments made by Mr. John Pattinson*, 1000 cubic feet of gas, along with 4·63 lb. of naphthalene, consumed in the albo-carbon lamp, yielded as much light as 2700 cubic feet of gas burned in fairly good flat-flame burners, or 1780 cubic feet of gas in argand burners of good construction.

* Trans. Newcastle Chem. Soc. 1882, v. p. 135.

Elster* found that 1 cubic metre of Berlin gas, carburetted with 53 grams naphthalene, yielded 20-candle gas, the hourly consumption per flame being about 100 litres and 5 grams naphthalene. Street-lamps consumed from 110 to 117 litres of gas along with 5 grams naphthalene, and yielded 16 to 17 candles. On the average the albo-carbon light gave an economy of 50 per cent. in gas, and of 30 per cent. in total cost. The best effect was produced with small burners. The specific gravity of the gas was raised from 0·38 to 0·60 by the carburetting process.

Fig. 107 shows the most usual shape of albo-carbon lamp. The copper ball *a* is fixed on the socket *c* by means of a stem, *b*, the joint being made merely by true boring-out of *c* and turning *b*; *a* is closed by a screw-cap, *d*, which serves for charging the naphthalene. The gas enters the ball through *c*, *b*, and *e*, and the burner *i* through *f*, *g*, *h*.

Fig. 108.



Above *i* is fixed the copper disk *k*, which is seen from above in fig. 108. It will be noticed that by moving the slide *l l*, which revolves about a pivot in the centre, the disk *k*, cut out to correspond with *l l*, is either closed or opened.

The burning gas from *i* heats *k*, which transfers its heat to *a*, and heats the naphthalene contained therein a little above its melting-point, say to 80° or 90°. In consequence of this the gas passing through *a* is charged with naphthalene vapour, which greatly increases its illuminating-power. If too much vapour is carried along and the flame begins to smoke, the slide *l l* is moved as in fig. 108, whereby the heating of *a* is greatly diminished.

In spite of the advantages justly claimed, according to all appearance, for the albo-carbon light, the progress which it has hitherto made, although not inconsiderable (at one of the largest English tar-works the author was informed that in 1886 they made 400 tons of naphthalene sticks per annum for this object), is yet far from being so universal as might be expected; and it has even been abolished again in some cases where it had been introduced. This seems to be mostly owing to the trouble caused by the lighting of the gas. At the commencement, before the naphthalene has become heated, the light is inconveniently small, and some patience is necessary. On the other hand, if the appa-

* Schultz, 'Steinkohlentheer,' 2nd ed. i. p. 199.

ratus is allowed to get too hot for one moment, the whole room is for a long time filled with the extremely pungent smell of naphthalene vapour. Of course this can be prevented by careful attention, but such is only too often wanting in the case of the domestics to whom the light must be trusted.

The principle of carburetting gas by means of naphthalene is evidently most excellent for enriching very poor gas, such as is obtained by abstracting the benzol from gas by one of the processes mentioned on p. 31 *et seq.* Davis* mentions that such gas, from which 4 gallons of benzol had been extracted per 10,000 cubic feet, and which only possessed 9-candles power, was easily brought up to 20 candles by employing the albo-carbon light; whilst the consumption of gas for lighting a room 10 feet square was brought down from 23 to about 3½ cubic feet per hour. This process would also be adapted for making good illuminating-gas from the residual coke-oven gases (p. 58).

Phillip's Carbo-Oxygen Gas† means the combustion of naphthalene, dissolved in petroleum, in a current of oxygen. A lamp suitable for this purpose has been described by Carl‡; but this process seems to be too troublesome and expensive.

J. W. Sutton (B. P. 4747, 1883) has constructed a somewhat similar apparatus; so also has W. G. Little (B. P. 17108, 1885).

Sudheim and Koppen (G. P. 6051 and 7784) employ naphthalene in the manufacture of non-phosphorus *matches*.

"*Pantopollite*" is dynamite containing a few per cent. of naphthalene. It was supposed to suppress the formation of nitrous fumes during the explosions; but practical trials have shown that the smell remaining after the explosion was far worse than in the case of ordinary guhr-dynamite§.

S. Stein (G. P. 23947) makes *porous stoneware* by incorporating with the clay naphthalene suspended in water or suitably dissolved, drying, volatilizing the naphthalene and recovering it at the same time, whereupon the clay is burned in the usual manner. The burned articles show an even porosity; and as the naphthalene does not leave any ash, the pores are not partly filled up with a fusible mass, less capable of resisting changes of temperature.

M. E. Contin‖ makes a specially "*detergent*" *soap* by melting

* Journ. Soc. Chem. Ind. 1886, p. 5.
† Wagner's Jahresb. 1870, p. 728. ‡ Ibid. 1872, p. 856.
§ Ibid. 1876, p. 495. ‖ Journ. Soc. Chem. Ind. 1884, p. 353.

two parts of ordinary soap with three parts of naphthalene. [While it is very doubtful whether such a soap will remove dirt better than the ordinary article, it is certain that those using it will produce an intensely disagreeable atmosphere around themselves!]

Naphthalene is sometimes employed for *keeping out vermin* (*e.g.* moths) and in stuffing animal-skins; Pelouze* recommends it for disinfecting purposes generally; Fürbringer† especially for water-closets and sick rooms, in lieu of carbolic powders. A special investigation of the antiseptic powers of naphthalene has been made by Ernst Fischer‡. It stops the development of mould and kills the fungi in a very short time, as *Penicillium, Mucor, Phycomyces, Oidium lactis*, the fungus of yeast, the different Schizomycetes, &c. Lower animals are driven away or killed; naphthalene therefore serves against moths, *Phylloxera*, the insects destroying collections of beetles and butterflies, and any other vermin. Against itch a salve, consisting of equal parts of naphthalene and vaselin, does good service. Naphthalene is excellent in the dressing of wounds; it serves equally well or better than carbolic acid or iodoform, and it is not poisonous like these. It seems therefore called upon to play an important part in medicine and in the household. [I have found that furs and woollen clothing, preserved against moths during the summer months by means of naphthalene paper, pertinaciously retain the penetrating smell of naphthalene, and require *long* airing before they are fit to be worn.]

* Bull. Soc. Chim. 1866, p. 351; 1868, p. 258.

† Berliner klinische Wochenschrift, 1882, No. 10.

‡ Schultz, 'Steinkohlentheer,' 2nd ed. i. p. 199.

CHAPTER X.

LIGHT OIL AND CRUDE NAPHTHA.

We understand by "light oil" that fraction of the first distillation of coal-tar which is midway between the first runnings and the carbolic oil. Some distillers term it "first light oils" or "crude naphtha." At some works, especially on the Continent, no such fraction is made, but every thing coming before the "middle oil," *i. e.* up to 170°, is collected in one receiver. The whole of this must then be subjected to the same treatment as will now be described for the "light oil" as defined above.

This oil contains a little benzene, more toluene, and much more of the higher homologues, together with phenols, naphthalene, and the unknown liquid oils occurring in heavy oil.

Light oil in this sense, if collected up to the point at which the distillate sinks in water, has the following properties. Its specific gravity is about 0·975; it begins to boil at 95° (the bulb of the thermometer dipping in the liquid); but only a little passes over before 120° is reached, from which point up to 171° about 30 per cent. distils. All that distils above this belongs to carbolic oil. But in order to form a correct judgment of the quality of light oil, the distillate up to 171° must be rectified. Thus a sample of not very superior light oil yielded in the first distillation:—

Boiling-point.	110°.	120°.	130°.	140°.	160°.	171°
96°	1	3	4½	9	16	26½ per cent.

And on rectifying the 26½ per cent.:—

Boiling-point.	93°.	100°.	110°.	120°.	130°.	138°.
90°.	1	2	5	9	13	16 per cent.

The light oil of trade is of course the more valuable the larger the proportion of easily volatile matters it contains, supposing it to be unadulterated coal-tar oil. Home-made light oil ought to give a good yield up to 171°, but little below 120°: the former proves that the receiver had not been changed too late for carbolic or heavy oil; the latter, that no first runnings have entered into the light oil.

A good deal of light oil is *employed as such*, without purification—*e. g.* for illumination in excavations (where the smoke is of no consequence), for thinning down heavy oil or liquefying pitch to make "refined tar," and especially for preparing varnishes for wood and iron (p. 277 *et seq.*). Thenius* makes from it "varnish-oil" by treating it several times with potassium bichromate, manganese, and sulphuric acid, then with water, at last with caustic-soda liquor, and subsequently distilling. Thus a limpid oil of sp. gr. 0·880 is obtained, which does not turn yellow in the air and is an excellent solvent for resins like sandarac, mastic, or copal; so that superior varnishes for photographers and printers, cart-grease, lubricating-oil, &c., can be prepared with it, for which special prescriptions are given.

Most of the light oil *is rectified*, at first by direct fire; only at smaller works is steam used for this product. Along with this oil, either mixed with it or exactly in the same way, is worked up the oil obtained on treating the carbolic oil with caustic-soda solution, after removing the latter (p. 374).

The object of this first rectification cannot be exactly the preparation of commercial products; for this the composition of light oil is still too complicated. For similar reasons it was formerly believed that it did not pay to wash it chemically, except when it had been purposely collected up to the point at which it contains much carbolic acid; and frequently even then its last portions only were treated with alkali. Hence the usual object of rectifying it is, on the one hand, to obtain the most volatile oils (which belong to the same class as the "first runnings" and are treated along with these), and, on the other hand, to separate the heaviest oils which promise no further yield of benzol and go better to creosote or carbolic oil. Between these two a fraction necessarily remains which exhibits some of the characteristics of either. This is always put back into the still and distilled with

* Verwerthung des Steinkohlentheers, p. 62.

light oil; so that the latter is ultimately completely split up into the two products mentioned above, although in each single operation three products are obtained, which we call light-oil naphtha, secondary light oil, and residue. This leads almost universally to making two fractions in the distillation of light oil, and running the third product, as residue, directly out of the still. The question can only be, where to set the limits. Evidently, if the residue is to go to creosote oil the distillation must be continued till no appreciable quantity of light oil remains behind; and this indicates the limit between the second and third fractions. Where the residue goes to carbolic oil, not even the above is of consequence, since the alkaline treatment in any case separates the hydrocarbons contained in it. In the former case the usual test is, to work till the distillate begins to sink in water; in the latter case the thermometer is usually consulted (see below).

It may be more uncertain where to set the limit between the first and second fractions. Evidently this does not matter very much, since the second fraction is always redistilled. Some English tar-distillers go by the hydrometer, and change the receiver when the distillate shows 10 degrees "under proof" (*i. e.* sp. gr. 0·932), at which point about one fourth part of the light oil has distilled. The second fraction is collected till it begins to sink in water, which corresponds to another 25 per cent., sometimes to 50 per cent. of the light oil.

The first fraction ("light-oil naphtha" or "twice-run naphtha") from light oil obtained in the first distillation of tar shows, for example:—

	Boiling-point.	Per cent. distilling at								
		23°.	100°.	100°.	120°.	130°.	138°.	149°.	160°.	171°.
1.	92°	...	½	2½	9	20	33	50	64	78
1*a*.	84	2½	5	12	24½	33	39	...	...	
2.	107	...	...	1	5	17	29	47	64	79
3.	104	...	...	½	3	10	21	44	63½	78
3*a*.	98	...	4							
4.	101	...	...	4	19	38	52	68	79	90
5.	107	...	...	1	5	17	29	47	64	79

1 *a* is the result of rectifying the first 50 per cent. of 1; 3 *a*, that of rectifying. the first 50 per cent. of 3. According to this,

there are great divergencies in the intermediate products; but finally, in all cases, nearly 80 per cent. has come over at 171°. The distillations 1*a* and 3*a* show that from light oil toluene, xylene, &c. can be obtained, but no considerable quantity of benzene.

The oils taken off from sodium phenate naturally show rather higher boiling-points, as proved by the following example, where 1 means the distillation of the oil itself, 2 the rectification of the first 41 per cent.

	Boiling-point.	Per cent. distilling at								
		93°.	100°.	110°.	120°.	130°.	138°.	149°.	160°.	171°.
1.	118°	...	...	...	...	6½	21	41	58	72
2.	...	...	...	5	15	25	32½			

Davis* quotes the following tests of "twice-run naphtha":—

	Spec. grav.	Per cent. distilling at					
		100°.	110°.	120°.	140°.	170°.	200°.
a.	0·878	0	17	41	72	94	99
b.	0·888	3	23	46	71	88	95
c.	0·901	2	20	40	62	80	90
d.	0·904	0	9	29	57	81	95

Stohmann-Kerl's 'Chemie' (vi. p. 1175) quotes the following statements from South-German (1) and North-German (2, 3) works:—

	Per cent. distilling at				
	100°.	130°.	140°.	180°.	200°.
1.	10·6	25·0	...	38·9	57·2
2.	15·4	...	22·5	44·0	
3.	20·3	...	27·12	50·0	

* Journ. Soc. Chem. Ind. 1885, p. 646.

No doubt the "light oil" in this case comprised both first runnings and our light oil together.

Already from these laboratory tests it is evident that the distillation of light oil is best guided by the thermometer. The first fraction might be made up to 170° and worked along with the first runnings from the tar; the second fraction is made at 205° or 210°, the product reworked, and the residue run to carbolic oil. According to Wurtz * the fraction of coal-tar distilling between 150° and 200° (roughly corresponding to our light oil) is worked up thus:—

First Rectification.

a. Fraction up to 120°, goes to the corresponding fraction of the principal distillate, received up to 150°.

b. Fraction between 120° and 190°, is washed with acid and alkali, then rectified.

c. Residue (above 190°), goes to creosote oil.

Second Rectification (of the fraction *b*).

a. Product up to 120°, contains benzene and toluene, goes to the corresponding products from the first runnings.

b. Product from 120° to 127°, yields solvent naphtha No. I.

c. „ „ 127° to 140°, „ „ „ „ II.

d. „ „ 140° to 150°, „ „ „ „ III.

e. Residue, goes to creosote oil.

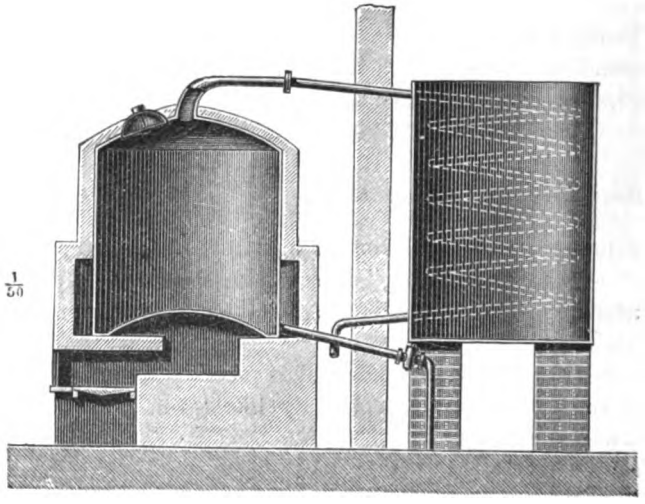
The product distilling from light oil at 170°–210°, and above called "secondary light oil," is sometimes employed for washing anthracene (p. 305); or it is chemically washed and rectified, so as to yield solvent naphtha.

The rectification of light oil takes place in wrought-iron stills, usually constructed and set exactly like tar-stills. The bottoms are, however, never made so much curved-in as shown on p. 215, because much less is left in the still when distilling light oil than when distilling tar. Only at the largest works are they made as large as the tar-stills; at others a small size suffices, as only a small percentage of the tar passes through them. *E. g.* a still 5 feet wide and 6 feet high suffices for four tar-stills of twice the height and width. It is preferable not to go below the size

* Dictionnaire de Chimie, i. p. 1633.

just mentioned, even at smaller works, but rather to work the still less frequently, or employ it at the same time for the first rectification of the crude benzol. The reason for this is that such a still, holding about 750 gallons, can be easily worked off in a working-day, say 7 to 9 hours, and allowed to stand overnight, to cool down the residue before running it out. The still-top is covered with brickwork or some non-conducting material. The still-head is made of cast-iron, and is connected with a 2-inch lead worm, ending in a 1½-inch lead worm, of which the lower part may be only 1 inch wide. A condensing-tub 4 feet wide and 6 feet high suffices for such a still. It should be separated by a wall from the still, as well as the two receivers for naphtha and secondary light oil; the discharge-cock best passes through the wall as well, so that all these parts are away from the fire and can be seen at a glance. Fig. 109 shows this arrangement.

Fig. 109.



The discharge-pipe for the residue can be provided with a screw-thread, in order to connect it directly by means of a pipe with the tank for carbolic or creosote oil. This is suitable, because the residue is very hot, even after standing overnight, and gives out very acrid and disagreeable vapours.

Of course the usual mountings must be provided, as man-hole, feed-pipe, air-vent, thermometer; a simple safety-valve (p. 414) is also advisable.

When *working a light-oil still*, a brisk fire is made at first; but this is moderated as soon as the distillation begins, and can be raised again later on. Here, too, some water comes at first, but ceases again after a short time. As long as naphtha comes over, say up to 150° or 170°, cold water must be run through the condensing-tub; but after this the water in the latter and the distillate must be allowed to get warm, because very much naphthalene comes along, and might choke up the worm if it solidified. We have seen (p. 414) that it is still more necessary to prevent this when distilling the oil taken away from sodium phenate. Special care should be taken to arrange the end of the worm so that the distillate can run out completely; otherwise, at the end of the operation a plug of naphthalene will be formed there, which might be overlooked in starting a new operation, and might lead to awkward consequences, especially in the absence of a safety-valve. It even happens, if the still is cooled down too much before discharging, that the residue solidifies entirely and cannot be run out without warming the still again.

Some manufacturers prefer heating the light-oil still by indirect steam; but this does not seem to offer any advantage. It is useful, however, already at this stage to substitute for an ordinary still-head a dephlegmating column, so as to effect a better separation of the product, as we shall see in the next chapter. This is especially advisable when first runnings and light oil are rectified together.

First Runnings.

This term is applied to the first and lightest distillate from the tar-still, as described on p. 227; and we shall now show how it is worked up. This fraction is sometimes called first light oils, or once-run naphtha, or crude naphtha, &c. Where no such fraction is made, but the light oil is collected all together, it is nearly always redistilled over a direct fire; and the "twice-run naphtha" or "light-oil naphtha" thus obtained is treated essentially as we shall describe for our first runnings.

This product contains of course the most volatile constituents of coal-tar, as enumerated in the second chapter; but along with

them, owing to the peculiar nature of fractional distillation, there are considerable quantities of less volatile bodies. Hence we find in it not merely benzene and its homologues, but sensible quantities of thiophens, of phenols, naphthalene, aniline and other bases, empyreumatic resins, &c. Some of the most volatile bodies are impurities to be removed as completely as possible, as methane homologues, thiophens, olefins, carbon bisulphide, mercaptans, nitriles. The "eupion" sometimes mentioned, and Mansfield's alliol, will have to be sought among the latter class of bodies.

Since a distinction or separation of all these bodies is not to be thought of, least of all for technical purposes, it is usual to estimate the quality of first runnings by fractional distillation exactly in the same way as described above (p. 423) for light oil, rectifying again the more volatile portion. The following table shows some of the results thus obtained, in percentages by volume:—

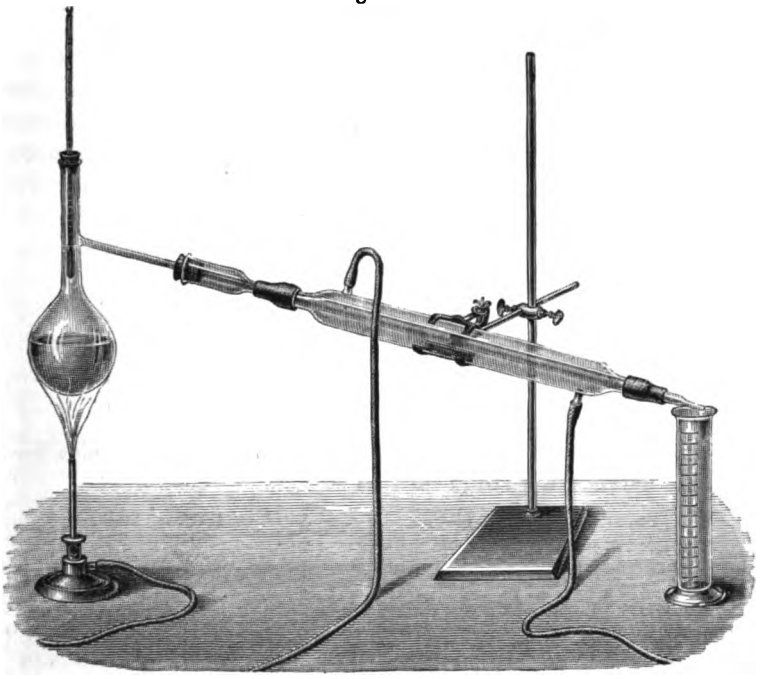
No.	Boiling-point.	88°.	93°.	100°.	110°.	120°.	130°.	138°.	149°.	160°.	171°.	Sp. gr.
1.	79°	1	2½	4½	12½	22½	31	37	45	52	62	0·906
2.	84	1	...	15	30	43	51	57	63	69	77	
3.	98	...	...	2	...	27	43	54	63	73	83	0·905
3*a*.	...	...	3	15	...							
4.	91	...	3	10	26	38	49	55	63	71	78	0·908
5.	89	...	½	5	34	45	55	61	68	73	78½	0·911
5*a*.	...	...	9	27½	40	47½						

In all these tests the thermometer-bulb at the beginning of the distillation was just immersed in the liquid; the "boiling-point" hence is much higher than the temperature at which the vapours actually passed over; and even the later temperatures are no doubt too high. 3*a* is the result of rectifying the first 45 per cent. of 3; 5*a*, that of the first 61 per cent. of 5.

The table shows that the composition of first runnings varies very much, especially at the lower temperatures, without being indicated by the specific gravity. In fact the latter is quite worthless for the estimation of the commercial value of crude naphtha. A single distillation of the latter does not suffice; and in any case that which has passed over up to 130° should be rectified. Even then the results differ very much if, as is usual in England, the thermometer bulb is immersed in the liquid, according to the size of the retort, the quantity of the liquid, &c. The only reliable plan is, to place the mercury-bulb at the height of the vapour-

delivery tube; and it is even preferable to work with a proper fractionating-flask connected with a Liebig's cooler (fig. 110); best of all with a dephlegmating head, such as Linnemann's three-bulb apparatus (comp. next chapter). It has been found the most suitable plan to place the mercury vessel exactly as figured here, that is, its top being at a level with the bottom of the side-tube.

Fig. 110.



More accurate methods for testing the value of crude naphtha will be described at the end of Chapter XI.

Good first runnings in the first distillation ought to yield at least 10 per cent. by volume up to 100°; in rectifying the product distilled up to 130°, at least 25 per cent. ought to come over up to 100°. Up to 171°, on an average 78 per cent. comes over.

Watson Smith found the following results of first runnings from Wigan cannel-coal tar (p. 263) :—

Below	130°.	130–140°.	140–150°.	150–160°.	160–170°.	170–180°.	180–190°.
Per cent.	15	20	10	6	9	7	11

Hohenhausen * quotes the following tests :—

A. *English Naphtha.*

Centigrade.	Wigan. per cent.	Yorkshire. per cent.	Scotland. per cent.
105°	...	4	...
110	4	16	17
120	19	34	38
130	33	47	49
140	45	...	58
150	55	...	69

B. *French Naphtha.*

Centigrade.	D'Anzin. per cent.	Blanzy. per cent.	Comp. Par de Gaz. per cent.
100°	5	14	10
120	24	37	23
130	39	49	55
140	50	59	75
150	60	69	90
160	67	77	98
170	75	85	

Davis (see below) quotes as the average of many examples from different parts of England :—

Sp. gr.	100°.	110°.	120°.	140°.	170°.	200°.
0·905	2	14	33	57	80	92

Washing with Chemicals.

The first runnings, as well as the light-oil naphtha, which is chemically quite analogous to it (comp. p. 425), is nearly always "chemically washed" before any rectification, *i. e.* treated with strong sulphuric acid and alkali, less frequently with oxidizing agents. The *functions of sulphuric acid* are :—combining with the bases; dissolving part of the thiophen and its homologues; destroying empyreumatic resins; dissolving olefins; generally, removing any bodies upon which it acts. Also naphthalene and phenols are converted into sulphonic acids remaining dissolved in the acid. Its action upon the valuable bodies, viz. benzene and its homologues, is very insignificant in the cold if the quantity of

* Journ. Soc. Chem. Ind. 1884, p. 73.

acid is moderate; but since its action in this respect is not=0, it ought not to be prolonged beyond necessity, and no excess over and above the quantity required for purification ought to be employed. Employed in excess, sulphuric acid forms "sulpho-oils," *i. e.* partly sulphonic acids, partly sulphones, *e. g.* $(C_6H_5)_2SO_2$, which to some extent remain dissolved in the hydrocarbons and are afterwards very troublesome, especially in burning. I have experimentally proved * that, under equal circumstances, the action of sulphuric acid in dissolving the benzenoid hydrocarbons is stronger in the case of the higher homologues than with benzene itself. When treated for five minutes with 5 per cent. of strong sulphuric acid, benzene loses 0·1 per cent. (when quite free from thiophen, even less), but xylene 0·25 per cent. The quantity of hydrocarbons dissolved increases with the quantity of acid employed and with the temperature. After being treated with sulphuric acid, benzene assumes a yellowish, toluene a greenish, xylene a pink colour; but all of these vanish after washing with water.

Only the strongest sulphuric acid of trade, the so-called rectified oil of vitriol, of specific gravity 1·84, can be employed; weaker acid dissolves the bases, but does not act upon the other bodies.

K. E. Schulze (communication to the author) has found in tar-acid, apart from the above-mentioned substances, acetone, methyl-ethyl-ketone, methyl cyanide, and a crystalline high-boiling substance, probably phorone.

The application of *alkali* (practically always caustic soda) in the case of first runnings, although indispensable, is less important than in the purification of petroleum, paraffin oil, or the heavier coal-tar oils, because the former contain a much smaller quantity of phenols, the removal of which is the principal object of this treatment. Hence some commence the washing with sulphuric acid, and end with weak caustic-soda liquor. The latter cannot be dispensed with entirely, as it must remove the remaining phenol and every remnant of sulphuric acid and sulphonic acids.

During the last few years it has become very usual, and seems more remunerative, to commence with the alkaline treatment. This allows of recovering the phenols, and is evidently quite indispensable when first runnings and light oil have not been separated in distilling, but are washed together before rectifying. It must be, moreover, borne in mind that the phenol contained in first run-

* Chem. Zeit. 1883, pp. 5 and 57.

nings is mostly real carbolic acid, and all the more valuable for this reason. On the other hand, it has been asserted that phenol made from first runnings alone has a very disagreeable smell, and very probably this is really the case; but this objection is avoided if the alkali, previously used for washing first runnings, is mixed with fresh caustic-soda solution and is subsequently employed for washing light oil or carbolic oil, as described p. 371. On the whole it seems advisable to proceed in this way; that is, to begin with alkali of, say, sp. gr. 1·15, follow with sulphuric acid of sp. gr. 1·84 (of which now decidedly less will be used than when commencing with it), and finish with a weak solution of caustic soda.

The mixing-apparatus for the chemical treatment of crude naphtha must of course be proof against the action of acids and alkalies. Usually it is made of wood lined with lead, the sheets of lead being burned together by the hydrogen-blowpipe. But at some places cast-iron vessels are preferred, which do not so frequently need repair as lead ones. Cast iron is but little acted upon by the strong vitriol, and is even less so when the latter is charged with tarry matters. Hence cast-iron machinery can be employed for agitation (mixing); and the discharge-cocks may even be made of brass or gun-metal, which would be impossible in the case of pure acid.

The mixers must be well covered over, to prevent the benzol from volatilizing during the operation. In the case of hand work this cannot be carried out so completely as with mechanical stirring, where the shaft passes through a stuffing-box and special pipes are provided for the running-in of naphtha, acid, water, and alkali.

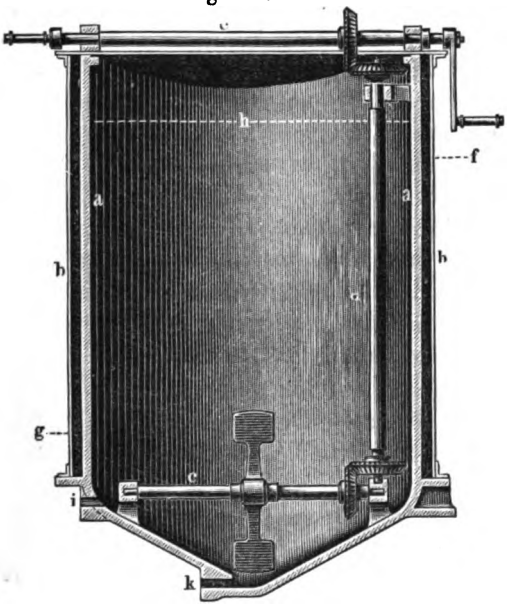
The discharge-cocks must be always so arranged that the dirty acid, as well as the water, can be run out to the last drop. For this purpose the bottom is made to slope to one side, and the cock is fixed in the lowest part in such a way that no portion of it projects upwards; so that any mixture of the liquids in running out can be entirely avoided with some little care.

At small works the mixing of the naphtha with the chemicals or the water can be done sufficiently by hand, especially as only a small percentage of the tar is subjected to it. This is done with wooden rakes, the head of which is about 15 × 6 inches and is perforated with six or eight one-inch holes; with these the attendant constantly fetches the acid &c. up from the bottom, which mixes

it much better than mere stirring. This should be continued for an hour, or for half an hour at least. In this case the mixer may be circular or square, whilst for mechanical mixing it should be circular. It should be only three quarters filled with the naphtha to be washed.

Evidently mixing by hand is very inferior to *mechanical mixing*, which is, indeed, preferred at all larger works. Sometimes it is done by a finely divided current of air (as described, p. 372, for carbolic oil); but most manufacturers prefer agitating by machinery, because the current of air might carry away some benzene. This cannot amount to very much, as the mixing need not last above

Fig. 111.

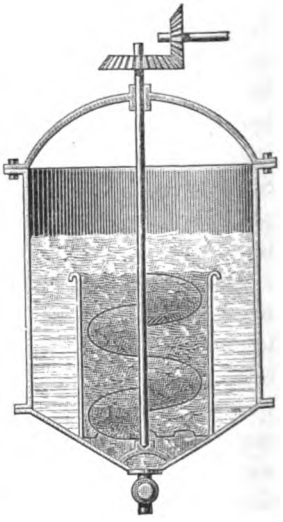


10 or 15 minutes. We shall mention only some of the most usual mixing-machines. We have already (p. 372) spoken of Hübner's machine, constructed like a churn, in which the mixing is effected by a perforated piston moving up and down, similar in principle to the mixing by hand with perforated rakes just described. A similar principle was employed in Jung and Must's apparatus*, but with the difference that the motion was not communicated by

* Described by Fuhst, Dingler's Journal, clxvi. p. 21.

gearing, but by a steam-cylinder placed directly on the mixer, the piston being attached to the same rod as the mixing-disk. Rolle's mixing-machine* consists of a sloping cast-iron cylinder, whose centre of gravity is situated in the agitating-shaft, provided with scoops for catching the acid and alkali, which, owing to their higher specific gravity, move at the periphery. This machine, as well as that constructed by Vogt†, seems less adapted for our purpose than either Hübner's or Jacobi's ‡. In the latter (fig. 111) the cast-iron cylinder, *a a*, is surrounded by a wrought-iron steam-jacket, *b b* (which can be dispensed with for naphtha, but is indispensable for carbolic acid, naphthalene, &c.), and has a conically shaped bottom. In this tapering part revolve the blades of a horizontal shaft, *c*, which is moved by a lateral vertical shaft, *d*, so that the contents of the mixer are quite accessible. In the arrangement shown in the diagram no stuffing-boxes are employed, because the packing could not be made to stand the action of acids, and the latter soon corroded the journals so that no tight joint could be effected. Lining with lead or asbestos packing did not prevent this in the case described by Jacobi, but I have seen several cases where it has been successful. The steam for heating enters at *f*; and the condensation-water issues at *g*; *h* shows the level of the liquid; *i* and *k* serve for discharging the oil and the washing-agents. The vessel *a a* should be cast in one piece, and with the bottom turned downwards, in order to avoid flaws, which would be very injurious in presence of the acid. The shaft *e* revolves 45 or 50 times, the agitating-shaft *c* 64 or 72 times per minute. This apparatus, which holds 3 tons, can be set in motion by two men, without any steam power, as the mixing only lasts a few minutes at a time.

Fig. 112.



A very efficient form of mixer is shown in fig. 112. Within

* Wagner's Jahresb. 1862, p. 680.

† Dingler's Journal, clxvii. p. 261; Jacobi (ibid. clxviii. p. 264) declares it to be quite useless.

‡ Dingler s Journal clxviii. p. 261.

the mixing-vessel there is a smaller cylinder, open at top and bottom, and in the centre there is a spindle, carrying an Archimedian screw. By the revolution of the latter the acid or alkaline liquor, which is always at the bottom, is raised up in the inner cylinder and poured out over the top thereof into the naphtha contained in the outer vessel. As it sinks down, it is caught up again by the screw, and thus a very good mixture is effected.

The mixer should be placed at a sufficient elevation to run both the acids and other liquids into suitable places. The dirty acid is sometimes emptied into carboys, but is usually carried away to an outside tank, by a lead spout.

The washing-water is not run straight away, as it is next to impossible always to prevent a little oil from coming along with it. This oil can be saved by the drain commencing in the mixing-house itself with a catch-pool, in which the washings are first collected. The floor is made to slope from all sides towards this catch-pool, so that any oil spilt anywhere can be washed into the pool. The liquid does not run into the drain from the top of the catch-pool, but through a pipe reaching nearly to its bottom, bent at an angle at the top and passing through its side into the drain. Since thus the drainage takes place from the bottom of the catch-pool, the oil remains quietly at the top, and is taken off from time to time.

The *operation of mixing* is performed in this manner:—When the naphtha has been pumped into the mixer, it is first allowed to rest quietly for some time; and the never-failing water, which collects below, is *completely* drawn off before adding the oil of vitriol, which would otherwise be diluted. A careful workman can, both in this case and in all analogous ones, run off the water without a drop of oil, by cautiously regulating the tap, observing the colour, and touching the liquid with his finger. If any oil should run off through some mishap, it is retained in the catch-pool.

The quantity of acid must vary according to circumstances, but not so much as might be imagined. A little over 1 lb. of oil of vitriol per gallon of oil suffices both for first runnings and light-oil naphtha (p. 425). If more is added, there is more loss of oils; if less, the distillates, especially the burning-naphtha, are discoloured by standing and contain naphthalene. Freshly distilled oils take less acid than old ones, in which more "empyreumatic

resins" are found. The above proportion is equal to 12 parts oil of vitriol to 100 parts naphtha by weight. It will be easily understood that the impurities are not completely removed by adding only so much acid as will have but a slight action upon benzene, toluene, and xylene. Hence, as the tar-distiller as a matter of course employs no more acid than is absolutely required, ordinary commercial benzol always contains such impurities as thiophen, its homologues, and even pyridine &c. These can only be removed by more energetic purification, as will be described hereafter.

With a mixing-machine, 10 or 15 minutes suffice for thoroughly working up acid and oil. After this at least an hour must elapse to allow the liquid to settle. It is best to mix at the end of the shift, and to let the liquid settle overnight, but not any longer, because otherwise the dirty acid turns so thick that it will not easily run out; sometimes great lumps of a pitch-like substance are formed, which choke up the tap. If the acid is too thick even after shorter settling, this is a proof that very many impurities were present—*e. g.* tar which frothed over into the first runnings, or light oil from the light-oil still. In such a case more acid ought to have been used, and more alkali will have to be used afterwards. Thus even previous mistakes of the men can be discovered afterwards. On the other hand, if the dirty acid is too thin, this is a sign that too much acid has been used, or that the water had not been completely run off previously. Neither of these ought to occur. Generally the acid will be found to have doubled its bulk by taking up tarry matters.

The acid must be run out to the last drop; and the bottom of the mixer must be constructed accordingly (p. 434); for any remainder of acid, on being diluted with the washing-water, separates again a large portion of the dissolved bodies and thus contaminates the naphtha over again, certainly more mechanically than by solution, as the tarry matters, when changed by sulphuric acid, are hardly soluble in naphtha. For this reason alone the *dirty acid* or *waste acid* (sometimes called *vitriol-tar*) must never be run off through the catch-pool and common drain (p. 437), which would be stopped up directly; it must be run by an open shoot into the main sewer, or, if it is feasible, directly into the river, or else into a special tank, or into carboys, casks, &c. Wooden casks last some time, as the corrosive action of the acid is greatly weakened by its tarry admixtures; but they are acted upon in time.

V. Falke* proceeds as follows in order to prevent naphtha from being carried away by the last portions of the acid in the form of an emulsion, and at the same time to avoid the contamination caused by adding water to the naphtha still containing acid. After having drawn off the first vitriol-tar, he agitates the naphtha for 15 minutes with 0·5 per cent. of sulphuric acid at 142° Tw., draws off this acid, and repeats the operation with acid of 106° Tw. By diluting the strength of the waste acid in this manner, it is possible to remove the last traces thereof with water or alkalis, without forming an emulsion.

When the acid has been drawn off, *washing with water* follows. Water amounting to about one fifth of the bulk of the naphtha is run in, mixed up with it for a quarter of an hour, and allowed to settle for half an hour. The water, which has now acquired a deep red colour, is run off by the bottom tap, every precaution being taken against oil coming along with it, and flows away through the catch-pool sunk in the floor of the house (p. 437). This operation is repeated three or four times, and, if the fourth water is still coloured, even a fifth time. Even the fifth water tastes rather bitter, perhaps from naphtha; it may also react very faintly upon litmus; but it ought in no case to show any colour.

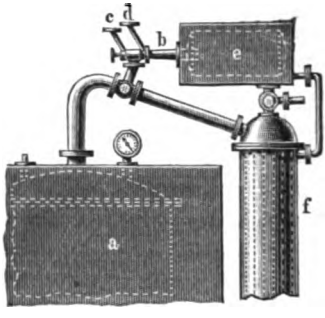
Now comes the *alkaline treatment.* The caustic-soda solution may be dilute, sp. gr. about 1·100. Its quantity cannot, like that of the acid, be fixed beforehand, but differs in each operation between 1½ and 6 volumes of that dilute solution for 100 volumes of tar-oil. If, as is now usual, there had been an alkaline treatment before the acid treatment, there is much less alkali needed for this last operation than has been just indicated. The liquor is gradually added during the agitation, until a change of colour has taken place in the tar-oil, when nothing further is added. Usually the colour changes from reddish brown to light brown or brownish yellow, and that very abruptly; but sometimes blue or purple colours are observed. Finally the liquids are well mixed up, and then left for an hour to settle; the caustic liquor is drawn off from the bottom; the naphtha is twice washed with water, and is now ready for distillation. In Lancashire sometimes milk of lime is used instead of caustic soda.

H. Hirzel (G. P. 34315) combines the distillation of the oils with the chemical washing in one operation, by intimately mixing

* Chem. Zeit. 1885, p. 1869.

the vapours of light oil &c. with the chemicals (acid, caustic liquor) in the state of a spray. In fig. 113, *a* is the still, *b* the injector (spray-producer), *c* the pipe conveying the steam, *d* that conveying the chemical agents, *e* the preliminary water, *f* the proper condenser. This process has not met with any extensive application.

Fig. 113.



The *loss in chemical washing* amounts on an average to 8 per cent. by volume of a mixture of first runnings and light-oil naphtha. Good oils lose only 5, or even 4 per cent., bad ones as much as 12 per cent. Fresh products require less chemicals than old ones, and lose less by the treatment. Careless working, where much naphtha runs away with the water, may double or even more than double the loss; and even the catch-pool does not quite prevent this, as some of the naphtha remains suspended in the water.

When testing purified naphtha by distillation, the boiling-points are usually found rather higher than those of the unwashed naphtha. This proves that the removal of less volatile bodies (phenols, naphthalene, bases) is more than compensated by that of more volatile ones (methanes, olefins, sulphur compounds). Complete purification, so that nothing but benzene and its homologues remain, cannot be expected; carbon bisulphide especially remains, often in very appreciable quantities; and even the "chemically pure" descriptions of benzene, toluene, &c. formerly, till Victor Meyer's discovery of thiophen and its homologues, contained these substances without anybody being aware of it (comp. p. 438).

The mixing-apparatus is best fixed in the same room as the steam-stills with their receivers and the receivers of the benzol-still (see below). Considering the great danger of fire, this building ought to be constructed without any wood, with an iron roof (for

instance, one of corrugated sheet-iron). The roof should be provided with movable ventilators; and the windows ought to be provided with iron shutters, which can be tightly closed from without with the least possible delay. Open fire (even matches) ought never to be tolerated in this room; it ought to be lighted by reflectors from without* or by electricity. Inside and outside hydrants and hose ought to be provided, so that every place may be reached by a jet of water. It has been observed that pure water is not very suitable for putting out fires of light tar-oils, because these float on the top; but ammonia-water, which is always at hand, does excellent service in this way, probably owing to the volatilization of ammonium carbonate and sulphide†; and putting on sand, ashes, and the like acts better than water. The safest plan would be to have one or more pipes leading from the steam-boiler into the room, through which it could be filled with steam by taps or valves *accessible from the outside*; thus the air would be driven out and the fire quenched; but there must be a large volume of steam, and it must issue in several places all over the room.

The washing process described above is probably that generally employed, that is, washing first with alkali, then with sulphuric acid, and again with a little alkali. The employment of the other processes, now to be mentioned, seems to have been discontinued.

Mansfield used, for every gallon of benzol, $\frac{1}{2}$ lb. of sulphuric acid and one ounce of nitric acid of spec. grav. 1·30, sometimes also a little bleaching-powder and hydrochloric acid. For toluene he took $\frac{3}{4}$ lb. sulphuric and $\frac{1}{4}$ lb. nitric acid. For the alkaline treatment he took lime-water or caustic-soda solution. The less

* A case has come under my cognizance, and has been described by me (Dingler's Journal, vol. cclix. p. 138), where, in a petroleum-refinery, the vapours issuing from a hot still, after the man-hole had been taken off, escaped in such quantity that an explosion was caused by their taking fire on a lamp, burning outside the building, at a distance of 20 feet; the "flashing" caused the fire to be propagated back into the building, which was altogether burnt down.

† I noticed this many years ago, also in my German work on tar-distilling, published in 1867 (p. 101). Some time later Mr. Watson Smith made the same observation, and strongly recommended the use of gas-liquor (to be stored in close tanks and provided with suitable piping and forcing power) for extinguishing fires in cotton-mills. Strong ammonia liquor has been also recommended for putting out petroleum fires by a Committee of the Munich Polytechnic Society (Färberei-Muster-Zeitung, No. 26, 1882; Journ. Soc. Chem. Ind. 1882, p. 351).

volatile hydrocarbons were boiled for 5 or 6 hours with a quarter of their volume of caustic-soda solution, sp. gr. 1·130, with reflux of the distillate; the liquid was then distilled and purified by dilute sulphuric, nitric, or hydrochloric acid.

Ronalds and Richardson prescribe twice treating with sulphuric acid, mixing for several hours, whereby much heat is evolved (probably by excessive action), washing with water and ultimately with lime-water or dilute caustic soda. They warn against allowing the light to act upon fresh naphtha, because in that case the water will not readily settle down.

Young* treats with bleaching-powder, adds dilute hydrochloric acid gradually, and at length caustic-soda solution; the oxidized products collect at the bottom as a black layer, from which the clear oil is easily drawn off. In this way the tar from gas-works in which the richer Scottish cannel coals are used is asserted to be advantageously converted into the ordinary products of the paraffin-oil industry (?).

According to Breitenlohner's experiments with peat-tar oils† the employment of oxidizing agents, as well as lime in lieu of caustic soda, leads to so much inconvenience that, after all, sulphuric acid and caustic soda must ultimately be resorted to.

Utilization of the Waste Acid from washing Tar-oils (Vitriol-tar).

The specific gravity of the dirty acid is about 1·365; and it generally contains as much acid as corresponds to about 45 per cent. rectified oil of vitriol. It is for the tar-distiller the most troublesome waste product imaginable, killing, as it does, all fish in canals, brooks, and rivers, and perceived at great distances by its stench and the red colour of the water. Of course distillers have always incessantly tried to work it up in some way, even without any profit. That this is no easy matter seems proved by the fact that in *none* of the tar-works visited by me in 1880 had any use been found for this acid, and that it was everywhere allowed to run away or sink into the ground somehow. In any case it ought first to be neutralized with lime.

If such tar-acid is diluted with its own bulk of water, most of the impurities rise to the surface as a tough, tarry substance of

* Hofmann's Report by the Juries, 1862, p. 140.

† Dingler's Journal, clxvii. p. 378.

most disagreeable smell, and can be skimmed off. This matter does not occupy much bulk and can be got rid of by burying it in the ground, or, wherever the sulphurous acid is of no consequence, by burning. It dissolves in alcohol with a fine red colour, but is insoluble in benzene or naphtha. Perhaps some useful colouring-matter might be extracted from it. The following patent describes other uses to be made of it.

This patent, taken out by W. P. Jenny in Germany (No. 3577), refers to the vitriol-tar from the washing of petroleum; but if it is at all useful, it must also apply to our case. According to one method the acid is to be diluted with its own bulk of water; the tarry oil precipitated is to be washed several times with boiling water, and at last with a little soda. It is then distilled up to 250° and the residue in the retort treated for 48 hours with a current of air. The oxygen is absorbed with avidity; and a mass is formed which, after cooling, forms a dark-brown resin. According to the other method the dirty acid is heated to 100° or 150° for several days, till a sample sinks down in water. It is then poured into water; and the precipitated substance is washed with much water; or else its own bulk of petroleum spirit is first added, in which case the mixture floats at the top. The product is more or less hard, according to its degree of oxidation, and is insoluble in water, alcohol, and alkalies, but soluble in all fats and oils, naphtha, benzene, &c., as well as in the strongest sulphuric acid. Melted up with indiarubber or guttapercha in different proportions, it forms an elastic body which can be used as an insulator; dissolved in light petroleum spirit, it yields a serviceable asphalt varnish.

The dilute acid remaining behind is still red or brown, and disagreeably smelling, as it still retains some of the tarry substances, especially all the bases (pyridine &c.), and sulphonic acids. It has been proposed to employ it for decomposing the carbolate of soda (p. 376); but it is not suitable for this purpose since, besides the colouring-matters, the sulphonic acids and bases would spoil the carbolic acid. It may, however, be used for making superphosphate, and in this case the tarry substances might do some good by protecting roots against insects &c.; it has been used for this purpose in Scotland. Small quantities might be got rid of by making sulphate of iron or copper.

At Young's paraffin-works near Edinburgh, the vitriol-tar was

formerly evaporated to dryness and the residue burnt. The sulphuric acid is thus converted into sulphur dixoide, which was utilized in vitriol-chambers. In the great majority of cases no vitriol-chambers are at hand; but the vitriol-tar might still, without dilution, best, perhaps, mixing it with sawdust, be converted into sulphur dioxide by heating in iron vessels, and that compound be utilized for preparing sulphites or hyposulphites (thiosulphates), or for other purposes.

This proposal (made in the first edition of this work) has been strongly recommended in the Chemiker-Zeitung (1885, p. 777). Attention is there drawn to Roessler's proposal for producing copper sulphate by the action of SO_2 and air upon copper (G. P. 22850), and to the employment of SO_2 for decomposing sodium phenate (comp. p. 377). For the last-mentioned purpose the empyreumatic substances are to be removed by washing the gas first with water, then with sulphuric acid, and then passing it through cylinders filled with freshly-ignited charcoal. A Körting's injector aspirates the gas and forces it through the solution of sodium phenate. After separating the carbolic acid from the solution of sodium sulphate, the latter can be reconverted into caustic soda by boiling with lime, and the calcium sulphite can serve for evolving more sulphurous acid, while the caustic soda is used over again for extracting the carbolic acid from crude carbolic oil. Thus the soda would not be lost, and the loss of carbolic acid, dissolved or suspended in the solution of sodium sulphate or chloride, as formed in the ordinary process, would be equally avoided.

The most important use of the waste acid, which at some works permits of disposing of it entirely to great advantage, is that for making *sulphate of ammonia*. This has been done to a certain extent for a long time past, and I have proposed it myself in the first edition of this work, for the acid previously freed from most of the tar by the addition of water. But this makes the acid inconveniently dilute, and most works consequently declined to do it. In the raw state the acid cannot be used directly for the manufacture of sulphate of ammonia, because the nauseous tarry substances would make the latter product unsaleable. There is, however, a way out of this difficulty, which has been used at several works for some time, every one of them holding it to be a secret not known to anybody else. By employing vitriol-tar for absorbing ammonia, and carefully skimming off the scum collecting in

the ammonia saturators, nearly all the tarry impurities can be removed, and a good sulphate obtained. These tarry oils are then worked into the creosote oil, or else they are burned; they contain the bases of coal-tar; and would be a very concentrated form of obtaining them, if ever there was any technical use for them. Undoubtedly that time will come; we need only point out the uses of quinoline!

A very important feature, as yet unknown to most tar-distillers, is the following:—It is well known that sulphuric acid containing any considerable quantity of arsenic cannot very well be used in the manufacture of ammonium sulphate, as in this case arsenious sulphide is formed which discolours the sulphate. For this reason most English ammonia manufacturers employ brimstone acid, although its price is very much higher than that of pyrites acid. But the latter can be used quite as well, if, during the saturating process, a certain quantity of vitriol-tar is added to it. The scum formed from the latter carries the arsenious sulphide up to the top, whence it can be skimmed off, and leaves perfectly white sulphate behind. I have seen this done on a very large manufacturing scale at a Dutch works.

A somewhat similar but much more elaborate and complicated process for dealing with vitriol-tar is the following, patented by the Chemische Fabriks Aktiengesellschaft in Hamburg (B. P. 9614, 1885; G. P. 34957 and 36372).

The vitriol-tar, in order to prevent further change by oxidation on standing, is, immediately after being drawn off, diluted with water up to the point at which the major part of the tarry matters is separated, and the dark-brown acid liquor below shows a specific gravity = 1·20 to 1·25. The separation is facilitated by adding some anthracene oil or crude carbolic acid, in order to liquefy the tarry matters. The upper layer is freed from acid by ammonia gas or ammoniacal liquor, is filtered from the aqueous solution of ammonium sulphate, and can be employed for impregnating or painting timber. The dilute acid at 1·20 or 1·25 can be obtained colourless by once more agitating with tar-oils or carbolic acid. It is usefully employed for a first washing of crude naphtha, in order to remove the organic bases, before washing with concentrated acid. For this purpose an excess of the dilute acid is employed; the acid solution of the tar-bases is diluted with ammonia, whereupon an upper layer separates which contains the impurities

and the free tar-bases which can be recovered by distillation. The ammonium sulphate is recovered by evaporation. Thus the acid of the vitriol-tar is utilized for manufacturing ammonium sulphate, whilst recovering the bases and the tarry substances formed by the action of the sulphuric acid, without any expense for chemicals. The upper layer, when treated with much water, yields to it sulphonic acids, while hydrocarbons, similar to the higher-boiling tar-oils, are left behind.

Treatment of the washed Naphtha.

This can take place in various ways. Some distil the product at once by steam, and collect the distillates as benzol, solvent naphtha, &c.; others interpose a distillation by direct fire and fractionation. The former process seems at first sight shorter and simpler; but it is advisable only when time presses, since by this plan the last products, especially the burning-naphtha, cannot be kept from discolouring in the course of time. This can be easily prevented by employing the second process, *i. e.* distilling once more over a direct fire, and making two or three fractions.

This is done in a still exactly like that used for light oil (p. 428); for the sake of cleanliness, it is advisable not to employ the light-oil still itself, but a special *crude-benzol still.* Its worm is made of lead, and, on account of the great volatility of benzol, is rather long. The still and its worm are placed under a shed outside the mixing-house; but the three receivers are either placed inside the house, or at least connected with it by pipes so as to be accessible from within. They consist of well-riveted iron boxes with a man-hole and a small hole for running in the distillate from the worm; the latter hole must just fit the pipe, and must be closed by a plug except when in use. This is done both on account of loss by volatilization and of danger from fire, since benzene vapours, even very much diluted with air, take fire most readily.

In firing, the same principle is followed as usual—strong firing during the heating-up, to be moderated immediately when distillation commences. At first the cooling-water is run as fast as a 1-inch water-pipe will permit, so that the distillate runs off quite cold; only towards the end should it run out tepid.

The fractionation is regulated by the thermometer, which is always fixed in the still. This has the drawback that the attendant

must be depended upon for timely changing the receivers. But he can be easily controlled by distilling 100 c. c. from a glass retort with thermometer, and noting the quantities passing over at the desired temperatures; according to very many experiments made by the author, the same result is obtained as on the large scale. The volumes thus found are calculated for the quantity put into the still (as measured by an iron gauge-rod in the mixer, or in any other way); and the attendant is instructed to run so many inches depth into each receiver. If there are tables of the contents of each vessel, the whole, including the calculation, can be done in ten minutes. By this plan a thermometer in the still itself can be dispensed with altogether.

The fixed points of the fractionation must vary according to the desired final products. For 90-per-cent. benzol, the first fraction is made at 110°, the second at 140°, the third at 170°, and the still is then stopped. For 50-per-cent. benzol two fractions suffice, up to 140° and from 140° to 170°. The second fraction, as we shall see, yields next to nothing distilling below 100°, and thus serves only for naphtha. It is not advisable to go beyond 170°, as this would injure the quality of the last naphtha; it is better to allow the still to cool overnight, and to work up the residue eventually, together with light oil, to extract every trace of benzene homologues. The distillation of about 750 gallons lasts 8 or 9 hours, so that a still can be worked off in a winter day; it rarely needs cleaning.

The following table gives some idea of the quantities of the products obtained, in percentages by volume of the raw material:—

	Distillate up to 140° (first product).	Distillate from 140° to 170° (second product).	Residue in the still.
First runnings alone.....	60–61	15–17	20–22
Light-oil naphtha	30–33	40	
Mixture of both.....	48–52	22–26	

CHAPTER XI.

RECTIFICATION BY STEAM. FINAL PRODUCTS.

The last rectification of light coal-tar oils is always effected by means of steam, either indirectly applied (dry steam) or blown directly into the liquid. In the latter case the steam carries away a large amount of substances boiling at a higher temperature than its own (according to the principles explained, p. 229); and it is hence reserved for the last stage, after the indirect steam has exhausted its action. As a rule, the steam-stills are adapted to either. They also always possess some arrangement for partial condensation or dephlegmation, in order to effect a better separation of the final products.

The steam ought to have a tension of at least $2\frac{1}{2}$ atmospheres, preferably more. It should be, if not exactly superheated, at least completely dried—*e. g.* by passing it through a coil of pipes, or through a long and shallow iron box, surrounded by the waste heat of the boiler-fire.

We shall now first sketch two different systems of steam-stills, whose principal parts might be mutually exchanged, so that the dephlegmator of the second system might be attached to the first still, and so forth.

Fig. 114 shows a system found in operation at large English tar-works. *a* is the still, made of boiler-plate, cylindrical with flat bottom and convex top; *b b* is a wrought-iron jacket round the sides and bottom; *c*, a non-conducting casing of some sort for preventing the loss of heat; *d* and *e* are steam-cocks, *d* supplying the steam-jacket, *e* the perforated coil *f* inside the still; *g* is a self-acting water-ejector for the coil *f*. The pipe *h* serves for feeding the still with crude benzol, *i* for discharging the residue, *k* for carrying away the vapours. The latter pipe communicates by the

Fig. 114.

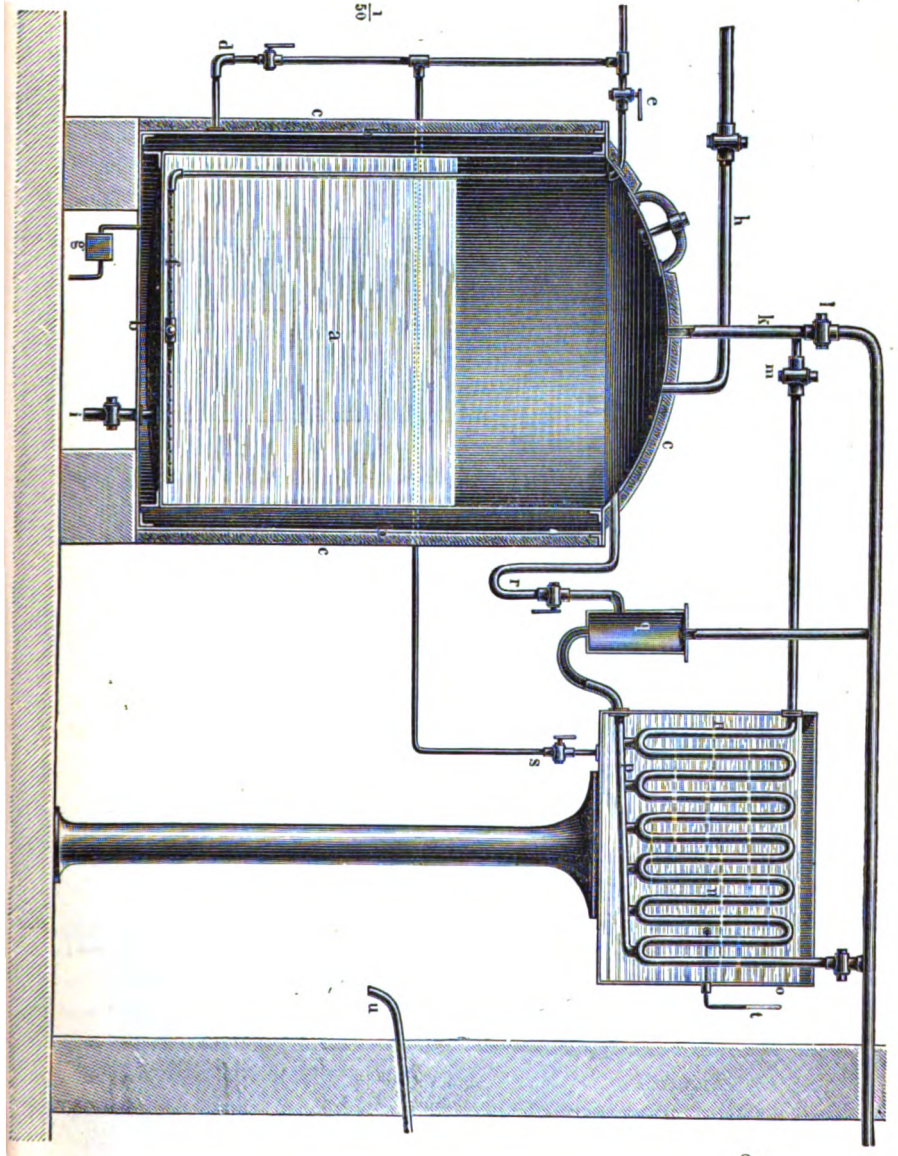
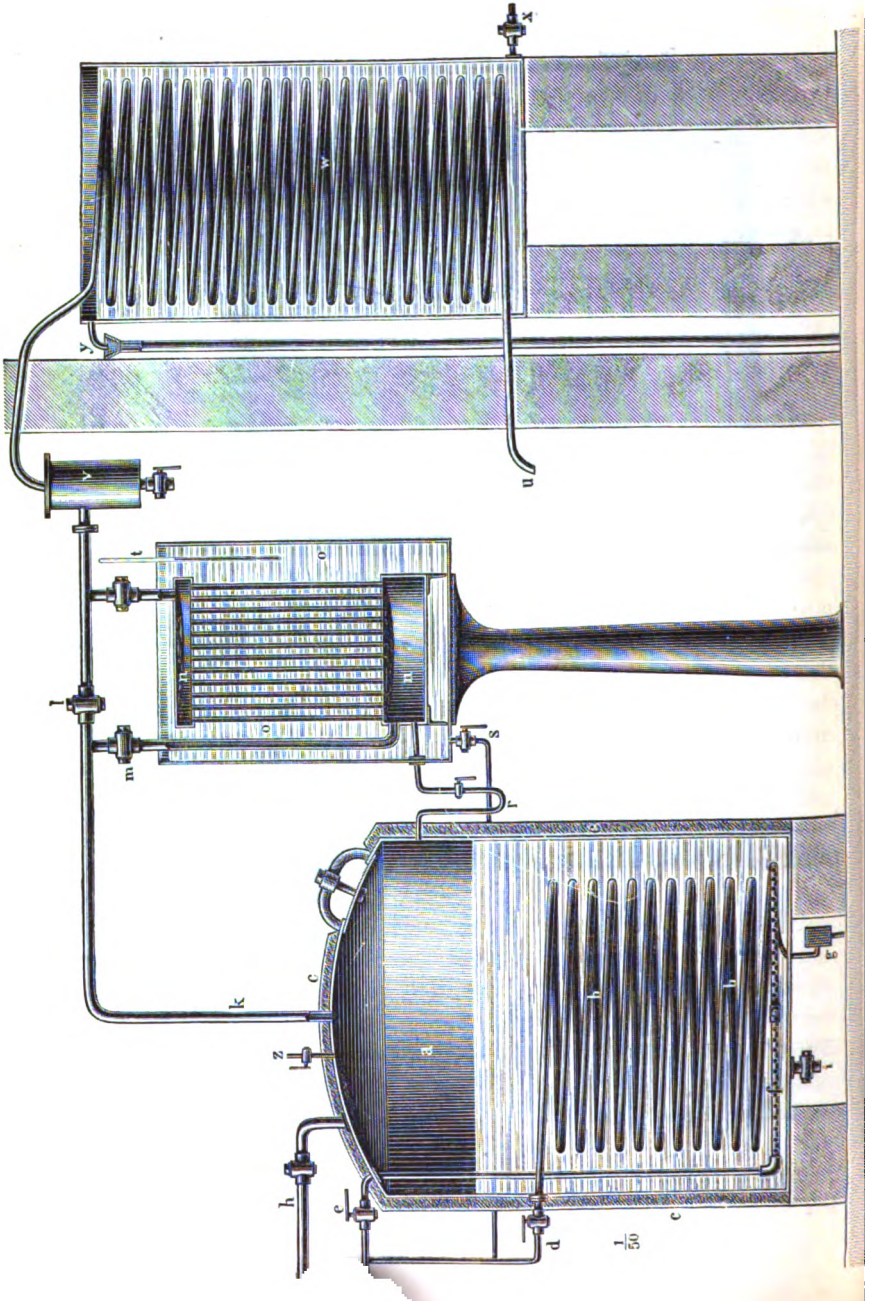


Fig. 115.



tap *l* directly with the worm, placed outside the still-house, or else, when *l* is shut and *m* is opened, first with the dephlegmator or "condenser" *n n*, made of lead or iron tubes. The latter is placed in the water-filled vessel *o*. The liquid condensing in *n n* collects in *p*, and flows through the vessel *q* and the hydraulic lute *r* back into the still. *q* sends a branch into the main vapour-pipe; but the bends of the pipes prevent the vapours from passing directly from *a* into *q* and thus into the worm. Through the steam-pipe *s* the water in *o* can be heated at will, this being regulated by the thermometer *t*. *u* is the bottom end of the worm, returning into the still-house.

In the second system (fig. 115, the similar or analogous parts being denoted by the same letters as in fig. 114), *a* is the still, indirectly heated by steam entering through the steam-cock *d*, which communicates with a leaden or wrought-iron coil *b* with water-ejector *g*. Direct steam can be blown in through the cock *e* and the perforated cross of pipes *f*. *h* is the feed-pipe, *i* the delivery cock, *k* the still-head. To carry the vapours away at once, the cock *l* is opened, when they first pass through the box *v* (for retaining any liquid carried over mechanically—a contrivance which should never be absent), and then enter the worm *w*, made of 1½-inch lead pipe, whose end at *u* returns into the still-house, where also the receivers are placed. The worm-tub is fed with water by *x*; at *y* the hot water runs off. If the vapours are to be dephlegmated, the tap *l* is closed and *m* opened. The vapours then enter the condenser *n n*, whose lower drum communicates with the upper one by fifty copper pipes of ⅜-inch bore. The condensed oil returns into the still by the hydraulic lute *r*: *s* is the steam-pipe for *o*, *t* the thermometer.

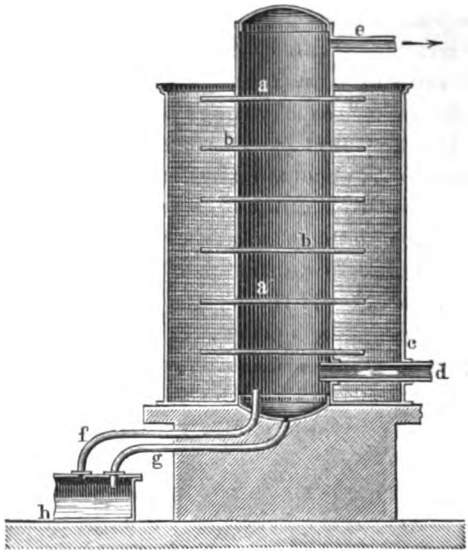
The second system appears to be superior to the first. Internal heating by a steam-coil is quicker and attended by less loss of heat than heating by a steam-jacket; and the dephlegmator represented in fig. 115 especially acts more thoroughly, and impedes the passage of the vapours less than that shown in fig. 114. Either is preferable to a simple worm, in which the ascending vapours are sometimes stopped by the backflow of condensing oils. Some manufacturers employ proper rectification-columns, as will be described later on in connexion with Savalle's apparatus.

C. Lührig (G. P. 26679) patents a zigzag pipe, surrounded by another such; the cooling water runs in the annular space opposite the course of the vapours; at each downward bend of the

pipe there is a branch pipe for taking away the condensed liquor.

C. A. Burghardt employs an inner cylinder, built up of tubes, *a*, separated by perforated plates *b* (fig. 116), made of wire-gauze, which being of greater diameter than the condenser, have their outer rims cooled by the water in the outer cylinder *c*. The vapours pass in at *d*, and are drawn through the apparatus by connecting the upper part at *e* with a draught. The condensed liquid flows by means of the tubes *f* and *g* into the receiver *h*. If that condenser is erected horizontally, the liquid condensing between the single plates *b b* can be drawn off in different states of purity (comp. Journ. Soc. Chem. Ind. 1885, p. 475).

Fig. 116.



Another condenser has been patented by L. & C. Steinmüller (G. P. 31238); it consists of a series of tubes, running parallel to each other in a horizontal direction, and cooled by a number of water-jets along their whole length.

The steam-stills are charged with washed naphtha either by means of a pump or an air-pressure apparatus, or else from a store-tank placed at an elevation, into which the naphtha has first been pumped. Meanwhile the air-vent (seen at *z* in fig. 115) is opened (it is either a tap or simply a 1-inch aperture), afterwards closed

by a cork or a screw-plug. Through this hole an iron gauge-rod can be introduced, in order to ascertain the level of the liquid in the still. The man-hole is only opened at longer intervals, for cleaning the still.

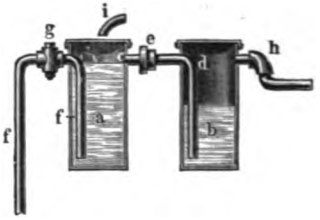
It is the rule to pump first the most volatile products into the still, and work them by indirect (dry) steam, then the less volatile products, which are first treated by indirect and afterwards by direct steam. If two products have been made in the benzol-still (p. 446), they are worked separately—viz. the second at once with direct steam, which can be done in a special still fitted merely with an arrangement for blowing in open steam; the distillation of the first product we shall now describe.

Steam is admitted with full force through the tap *d* into the steam-jacket or the steam-coil *b* (the letters refer to both figs. 114 and 115). As soon as the liquid begins to boil and to distil, the steam-cock is almost closed, and is then regulated so that the distillation goes on continuously but not too quickly, not to say tempestuously; otherwise there would be loss by incomplete condensation, and danger of fire. At first a little water comes over, which often makes the benzol quite turbid; but this need not be minded, as the benzol soon clears up, either in the receiver or in the store-tanks. Later on, when direct steam has to be used, of course very much water appears, which must be separated from the naphtha. This can be done by the apparatus shown in fig. 117, for instance, which at the same time permits the naphtha to be finally purified by dilute caustic-soda solution. Two open cylinders of tin-plate, *a* and *b*, 9 inches wide and 2 feet high, are each provided at the top with a channel, serving as a water-lute, into which a tin cover is put; they are connected by the two pipes *c* and *d*, which can be quickly joined or separated by the screw-cap *e*; *c* ends open 1 inch below the top of *a*; *d* bends down inside *b*, and ends just above its bottom. From the bottom of *a* the pipe *f* rises up, passes out, and leads to a waste-pipe; it can be shut off by *g*. From *b* the pipe *h* takes away any liquid just below the top. *g* and *e* must leave *a* exactly at the same level; *h* may be at the same or at a slightly lower level. At *i* the end of the cooling-worm is sketched.

Before starting, *a* is three quarters filled with water. As soon as the mixture of naphtha and water comes out of *i*, *a* is quickly filled up to the level of *c* and *f*, and its contents run out of these

two pipes; but as water and naphtha instantly separate, only naphtha will run away from the top (through *c*), and only water

Fig. 117.



from the bottom (through *f*). If *f* were below *c*, the former would fill entirely and act as a siphon, which should not take place. For use in case of need the tap *g* is provided; but this should never be required.

From *c*, the naphtha runs over into *b*, fills this vessel, and runs away into the receivers through *h*. At the last stage, *b* is half filled with dilute caustic-soda solution (sp. gr. 1·10), so that the naphtha must pass through it; why, we shall see later on.

At least *two receivers* are needed; these suffice, if the distillates are run or pumped straight from them into store-tanks; but some distillers prefer receiving the distillates in a large number of smaller drums, which facilitates the classing of the products. As receivers, instead of closed iron tanks, open vessels with loose covers are preferable, as these can be easily inspected and cleaned after each operation, so as to ensure that the final products are quite pure and colourless. In this case, since iron would rust quickly and the water would cause a red mud to be formed, wooden boxes lined with zinc or lead are employed, with their bottom sloping a little to one side, and a tap fixed at the lowest point, so as to draw off their contents completely, either into a store-tank or into a pump.

The usual process for separating the distillates is as follows:— First, as above mentioned, only indirect steam is admitted through the tap *d* (fig. 114 or 115). The most volatile products escape first; but from the first, along with benzene, a little toluene also distils, and later on much more, which is unavoidable in any fractional distillation, as explained, p. 229. But since in trade specific qualities of commercial "benzol" are required, means must be sought for obtaining these as directly as possible, with the least

possible quantity of intermediate products to be worked over again. For this purpose the principle of partially condensing the vapours, with reflux of the condensate into the still, is always employed, as was done long ago by Mansfield; this is the same as has long been known in spirit-distilling as "dephlegmation." It is effected by the condenser *n n*, in the vessel *o*. By closing the tap *l* and opening *m* the vapours arriving by *k* are compelled to enter *n n*, the water in *o* being heated by the steam-pipe *s* to the required temperature. For 90-per-cent. benzol the water-bath should be kept at 60°, for 50-per-cent. benzol at 70°–80°; but these temperatures cannot be absolutely fixed beforehand, and must be found out by experience for each apparatus; in any case they should be kept as constant as possible. The liquor condensing in *n n* returns through *r* into the still *a*; it is essentially toluene, with a little benzene. Some manufacturers allow it to run back into *a* directly and continuously (fig. 115); others interpose a small intermediate vessel (*q*, fig. 114), if the shape of the condensers makes it more advisable to allow the vapours given off in *g* to get into the main delivery-pipe. Others run the condensate from *n* into a separate closed receiver, in order to rectify it separately. The uncondensed vapours of benzene, with a little toluene, now enter the main vapour-delivery-pipe, then the worm *w*; and the benzol condensed therein runs through *u* and the separating-cans, fig. 117, into the receivers.

After some time, nothing further will come out of *u*; and now it is time to raise the temperature in *o*, to obtain weaker benzol. Usually it is possible, even for making pure toluene, to work with water in *o*, heating it to the boiling-point, Water is all the more applicable, if only 30- or 40-per-cent. benzol is to be made at this stage, which is the rule. At most tar-works, in the further distillation no separation into pure hydrocarbons is aimed at, and hence the dephlegmation is not carried further. When nothing further runs from the worm *w*, the condenser *n* is put out of work by closing the tap *m* and opening *l*. Now all vapours pass directly into *w* and are condensed, so that again a considerable quantity of distillate is obtained. Gradually this ceases: and when little or nothing comes over, the indirect steam from *d* is stopped and direct steam is injected through *e* and the apertures of *f*. Even with steam of only 2½ or 3 atmospheres an ample quantity of xylene, trimethylbenzenes, and some tetramethylbenzenes is carried over, which mixture we shall describe afterwards as solvent

and burning-naphtha. Xylene is now employed as such in the manufacture of colours, and is for this purpose separated in Savalle's column-apparatus (see below).

We must now see on what principles the fractionation takes place. It seems the simplest course to be guided by the thermometer in the still or in the dephlegmator; but as the first requirement is to obtain products fulfilling certain commercial tests, and it is not very easy to carry this out by means of the thermometer alone, other matters must be taken into account. We shall first describe the process carried on at a tar-works possessing a still with rectifying-column, and working chiefly by the thermometer. Distillation by steam is there performed *twice*. In the first distillation the following fractions are made:—

1st, up to 103° (thermometer in the still), yields 65–70-per-cent. benzol;
2nd, 103–110°, yields 30-per-cent. benzol;
3rd, 110–130°, yields nothing at 100°, 60-per-cent. at 120°;
4th, above 136°, yields solvent naphtha.

In the second distillation the dephlegmator has the principal work to do. By rectifying fraction 1 and keeping the dephlegmator at 56°, 90-per-cent. benzol is obtained; with the dephlegmator at 80°, 50-per-cent. benzol comes out. The thermometer in the still, as long as 90-per-cent. benzol comes, never exceeds 100°. When this temperature is obtained, fraction 2 of the first distillation is run in, and the temperature in the still is allowed to rise to 105°, that of the dephlegmator to 80°; the receiver is also changed, and 54-per-cent. benzol obtained. Now the receiver is changed again, open steam is injected into the still, and the distillate collected as solvent naphtha. It would be quite possible in the same apparatus to make pure toluene.

Other manufacturers are not guided by the temperature in the still, but only by that of the dephlegmator; and this seems preferable. It is certain that after some experiments with any special apparatus, and carrying on the previous operations on the same plan, the regulation of the temperature of the dephlegmator will by itself permit any desired product to be got; *e. g.* it will be possible to manage so that the whole distillate, when it is mixed up, shall yield 50-per-cent. benzol. The receiver will then be charged for the first time when nothing further passes through the dephleg-

mator, for the second time when indirect steam does not yield anything even after shutting off the dephlegmator; so that a third product is to be obtained by open steam.

None of these marks can be implicitly trusted to furnish products fulfilling distinct commercial requirements. Hence during the operations several laboratory tests must be made; and some manufacturers depend entirely upon these. The testing is done in a glass retort, or, better, in a fractionating-flask with Liebig's condenser (fig. 110, p. 432), taking as fixed points for the fractions only 100° and 120°, and for the later distillates also 130° and 160°.

In most cases a previous laboratory test of the charge in the steam-still will give an approximate idea how much of each fraction may be expected. The description given by Davis (comp. later on), along with the tables given by him, are intended to indicate beforehand how much of the different products can be run from the still. In accordance with this a sample is taken a short time before it is believed the receiver will have to be changed, after well mixing up its contents. Supposing 90-per-cent. benzol to be aimed at, if the test shows that the contents of the receiver just give 90 per cent. at 100°, of course the receiver must be immediately changed, since it cannot be expected that this strength will remain for any length of time if the distillation be continued. Properly speaking, the distillate ought to be always rather stronger than necessary before being pumped into the store-tanks, to make quite sure of its being sufficiently so. Before being pumped away, its height in the receiver is gauged, and the volume (to be ascertained by a table) and analysis are noted. It must now be brought to exactly the proper strength by adding a calculated quantity of the contents of the next receiver. Supposing this to be found = 70-per-cent. benzol, its contents will have to be divided among the store-tanks for 90- and 50-per-cent. benzol. The calculation is made in the following manner:—Supposing 120 gallons of 95-per-cent. benzol to have been pumped from the first receiver, and 160 gallons of 75-per-cent. benzol to be found in the second, the question is, how much of the latter must we pump to the former in order to obtain a commercial product of 90 per cent.? We shall learn this from the proportion:—

$$120 \times 95 + x \times 75 = (120 + x)90;$$
$$120(95 - 90) = x(90 - 75);$$
$$x = \frac{120 \times 5}{15} = 40.$$

That is to say, to the 120 gallons of 95 per cent. another 40 gallons of 75 per cent. should be added, to obtain 120+40 gallons of 90 per cent. The remaining 120 gallons of 75-per-cent. benzol are pumped into the store-tank for 50-per-cent. benzol, and both quantity and quality noted. Suppose now that the third receiver is found to contain, say, 144 gallons of 40-per-cent. benzol. We shall now put:—

$$120 \times 75 + 144 \times 40 = (120 + 144)x;$$
$$x = \frac{14760}{264} = 55{\cdot}9.$$

This means, if the whole contents of the third receiver be pumped to the 120 gallons of 75 per cent., the mixture will still be 56-per-cent. benzol, and will bear an addition from the contents of the next receiver. But the examples already given will suffice to show how the calculation is made for this or any similar case. Frequently the benzol in the tanks is kept rather above the standard, and is only brought down just before it is sent out; but care should be taken to do this invariably with the immediately following, not with any later fraction.

If no 90-per-cent. benzol at all is required, all the above-mentioned distillates would be pumped into the tank for 50-per-cent. benzol, always noting both quantity and quality. By multiplying each time the number of gallons by the percentage, and dividing the product by the total number of gallons, the percentage of the mixture will be found. The "percentage" in this case is no doubt only an apparent one; a 50-per-cent. benzol has no analogy with a 50-per cent. solution of a salt or with 50-per-cent. spirit of wine; but practice has shown that calculations like those exemplified are quite trustworthy. As a rule they make the product appear slightly below its actual strength; but this is a fault of which the buyer will not complain, and which the tar-distiller might easily correct if he cared to do so. In the case of

important contracts, of course such calculations will not be depended upon, but the mixture must be specially tested.

Hohenhausen * gives the following examples:—500 gallons of crude Yorkshire naphtha which before separation tested

At 110°	120°	130° C.
16	34	47 per cent.,

yielded, as the first portion, with dry steam 250 gallons 40-per-cent. benzol, testing

At 95°	100°	110°	120°
15	39	75	89 per cent.

Wigan crude naphtha, treated in the same way, tested :—

Sample A.

500 gallons crude.	At 110°	120°	130°	140°	150°
	17	38	49	58	69 per cent.
200 gallons obtained by dry steam.	At 95°	100°	110°	120°	
	14	38	73	89 per cent.	

Sample B.

500 gallons crude.	At 110°	120°	130°	140°	150°
	13	34	47	57	68 per cent.
260 gallons obtained by dry steam.	At 95°	100°	110°	120°	
	15	40	74	90 per cent.	

Besides 90- and 50-per-cent. benzol, frequently 40-, or even 30-per-cent. benzol is required in trade. What now comes, is mostly toluene, and is sometimes sold as such. Commercial toluol ought to yield 90 per cent. at 120°. But the next fraction after benzol is sometimes destined for *carburetting-naphtha*. According to a specification proposed by Dr. Letheby and adopted by several gas-works, such naphtha ought to yield at least 70 per cent. at 130° and 90 per cent. at 150°; its specific gravity ought to be 0·85–0·87. In practice, only the first point need be taken care of; the others will follow of course. This product essentially consists of xylene. The specific gravity proves the absence of any adulteration with petroleum spirit. When passing from benzol to

* Journ. Soc. Chem. Ind. 1884, p. 74.

carburetting-naphtha, half filling the second separating-can (*b*, fig. 117, p. 454) with weak caustic-soda solution should not be omitted. If there is no sale for this product, it is redistilled and split up into benzol and solvent naphtha.

According to a table given in Wurtz's 'Dictionnaire de Chimie' (i. 1663), French distillers would seem to fractionate in a different manner. The first principal fraction received consists of the tar-oils boiling from 30° to 150°. They are first redistilled in boilers of 2000 litres capacity by open fire or steam; two thirds are distilled off, and the residual third run to the second fraction, viz. the oil boiling between 150° and 200° (compare light oil, p. 427). The above two thirds are treated with acid and alkali, and rectified afterwards, the following fractions being made:—

a. Boiling from 30–70°, pentane, hexane, &c.
b. „ „ 70–100°, benzene and toluene.
c. „ „ 110–127°, benzine No. I. for removing grease.
d. „ „ 127–140°, „ No. II. „ „
e. Residue, goes to the second principal fraction.

But it is not possible to separate the hydrocarbons as easily and completely as is indicated in that place. None of the tar-works known to the author proceed in this way.

That which follows the weakest benzol, or the toluol, is received as *solvent naphtha*; and some manufacturers make no further fraction, but put to this also every thing obtainable from the liquid by direct steam. The name is derived from the fact that this product is used for dissolving india-rubber in the manufacture of waterproof fabrics. Of late it has been extensively employed in the manufacture of anthracene (p. 303); and it also serves for removing grease-spots. It consists principally of xylenes and trimethylbenzenes, no doubt also of other bodies not well understood. The india-rubber-manufacturers require the solvent naphtha to be entirely free from naphthalene, which may occur in small quantity in the last distillate by steam. Hence distillation should not be carried too far, but should be interrupted when the product yields 90 per cent. at 150° (some allow 160°), and its specific gravity does not exceed 0·875 at 15°. This will be the case with the whole as soon as a sample of the distillate, as it flows from the worm, shows 0·880 at 15°. Since differences in temperature cause very important differences in the specific gravity, to reduce the observed to

the normal temperature (which can be done by means of the table in the Appendix) should never be neglected.

If special stipulations are made for the delivery of solvent naphtha, and if, on the other hand, there is a sale for *burning-naphtha*, the last distillate is received as such. The operation is carried on up to the point at which the distillate begins to show a little colour. Then the steam is stopped at once, and the operation finished. If the washing has been well done, the distillate remains colourless, and the end of the distillation must be judged of by other tests. Smell is a very distinct and characteristic test, but necessarily subjective; naphthalene especially will thus be detected. Another criterion (in this case a certain one) is the specific gravity, which ought to be 0·900 for the last sample running out of the worm, or 0·880–0·887 for the whole of the naphtha. A further test is obtained by shaking up the naphtha; only opalescent beads, instantly vanishing, ought to be formed, and no remaining froth. Moreover it ought not to be discoloured when exposed to the sunlight for several days; it will then keep colourless in the dark for a long time.

The distillation of the 5- to 8- per-cent. burning-naphtha which can be got from the distillate up to 140 °C. of the benzol-still (p. 447) takes a comparatively very long time. Hence it is often preferred not to distil it at all up to this point, but to mix the residue, remaining after getting out the solvent naphtha, with the fraction from the benzol-still boiling from 140° to 170°, which is distilled at once by open steam and yields merely solvent and burning-naphtha.

In all distillations by open steam the box for catching any liquid carried over (*v* in fig. 115, p. 450) is essential for protecting the distillate from discoloration; it should be emptied at least once per day; the caustic liquor in *b*, fig. 117, p. 454, must also be daily renewed.

From the product distilled up to 140° may be expected 60 or 70 per cent. of 50-per-cent. benzol, 20 or 25 per cent. of carburetting and solvent naphtha, 5 to 8 per cent of burning-naphtha. The product distilled between 140° and 170° yields 25 to 50 per cent. best naphtha, 50 to 25 per cent. burning-naphtha, and 25 per cent. residue in the still, which it is best to pass through the light-oil still, although it generally sinks in water.

Most tar-distillers make only 90- or 50-per-cent., sometimes 40- or 30-per-cent. benzol, solvent and burning-naphtha. Only

exceptionally, and that mostly at the colour-works, is a *complete separation into benzene, toluene, xylene, &c.* aimed at. This can be effected by more perfect apparatus than those hitherto described, carrying out the principle of dephlegmation as completely as this has long been done in the rectification of spirit of wine. Mansfield proposed this already in 1847; but it seems that Coupier, in 1863, first carried it out for the purpose of isolating each of the hydrocarbons in a nearly pure state *. His apparatus is shown in fig. 118, on a scale of 1 : 50. A designates the lower reservoir (the still proper), to which is attached a steam-pipe (forming a coil inside), a man-hole, a discharge-cock, &c. B is the opening for feeding with crude benzol. The still is surmounted by the cast-iron rectification-column N, which will be described in detail below. The thermometer *t* is required for regulating the process. The heat of the steam-coil in A (the steam should be at a pressure of two atmospheres, or even more for the highest homologues) causes the liquid to boil. In the column N the least-volatile oils are condensed by the cooling action of the air and run back into A. The more volatile vapours pass into the trough D, where they are kept at such a temperature that the hydrocarbon of lowest boiling-point remains in the state of vapour, whilst all the higher-boiling ones condense and flow back into the still. For this purpose the vapours pass through the annular spaces of the condensers, placed alongside one another, whose walls are washed inside and outside by the liquid contained in D. If only benzene and toluene are to be separated in the pure state, the liquid in D may be water; for the temperature in D should be kept (by means of the steam-coil *m* and the thermometer *t*) at 60–70° for benzene (boiling-point 80°·5), and at 100° for toluene (boiling-point 111°). If xylene or trimethylbenzenes were to be obtained, D would have to be filled with a solution of ammonium nitrate (boiling at 164°) or with paraffin †. What condenses in the annular condensers G G runs back to N, through the pipes *a, b, c, d*, whose bends prevent the passage of vapours from N to G G. It will be seen that the liquid first condensed enters the column at a lower place than that condensed afterwards. The taps *r r* serve for taking samples and

* Bulletin de la Société industr. de Mulhouse, 1866, p. 260; Dingler's Journal, clxxx. p. 385.

† This would require steam of 6–7 atmospheres for the steam-coil in A; it is hardly ever done.

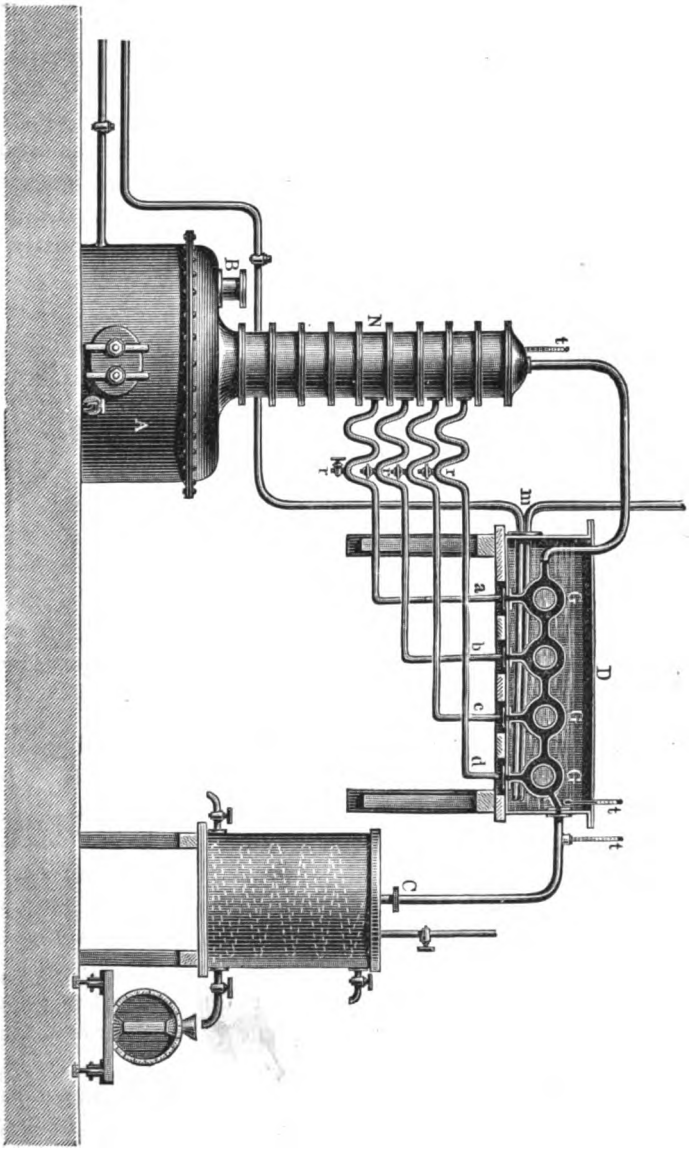
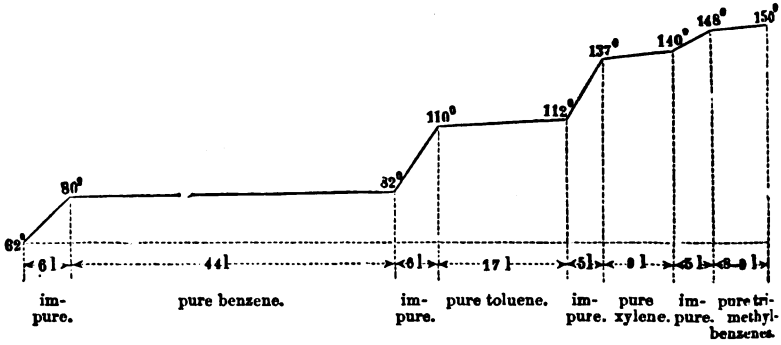


Fig. 118.

testing the operation. The vapours issuing from the last condenser pass into the worm C, where they are completely condensed. If crude benzol is distilled, the water in D is first kept at 60° or 70°. When no more benzene comes out of C, the receiver is changed, and the temperature in D raised to 100°. At first a little of a mixture comes over; but soon pure toluene appears, which requires steam of 3½ atmospheres in A. When this ceases, the operation is usually stopped; but in case of need, xylenes and trimethylbenzenes can be isolated in a similar manner. Coupier has shown by the following graphical diagram the quantity of

Fig. 119.



principal and intermediate products obtained by his apparatus from 100 litres of crude benzol, boiling from 62 to 150° (say ordinary commercial 50-per-cent. benzol).

Hence 44 litres pure benzene and 17 pure toluene are obtained, and also:—(*a*) 6 litres first runnings, consisting partly of carbon bisulphide, amylene, &c., which may be utilized by adding it to the solvent naphtha; (*b*) 6 litres of an intermediate product between benzene and toluene, which is redistilled; (*c*) about 27 litres high-boiling products, which formerly went at once into the solvent naphtha, but from which now the xylene (9 litres) is sometimes separated.

Figs. 120 and 121 show the plan and section of the compartments of the rectifying-column N (fig. 118) on a scale of 1 : 25. The vapours rise in the pipes *q*, but are checked by caps *r*, and must find their way through the apertures and the liquid

standing over them. That liquid, consisting of the portion of the vapours condensed by the cooling action of the air, gradually flows through the overflow-tubes *s* from one plate into another. The labyrinth-partitions ("chicanes") *p p* cause the gas to remain in prolonged contact with the liquid, so as to precipitate the less volatile oils from the vapours, and to carry away by the heat of the latter the most volatile constituents of the liquid. The frequent repetition of this process in the 9 or 10 compartments of the column causes the fractionation to be much more thorough than even repeated rectifications without them would have made it.

Fig. 120.

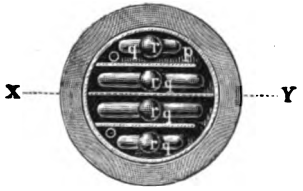
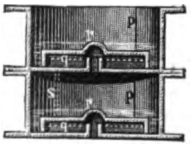


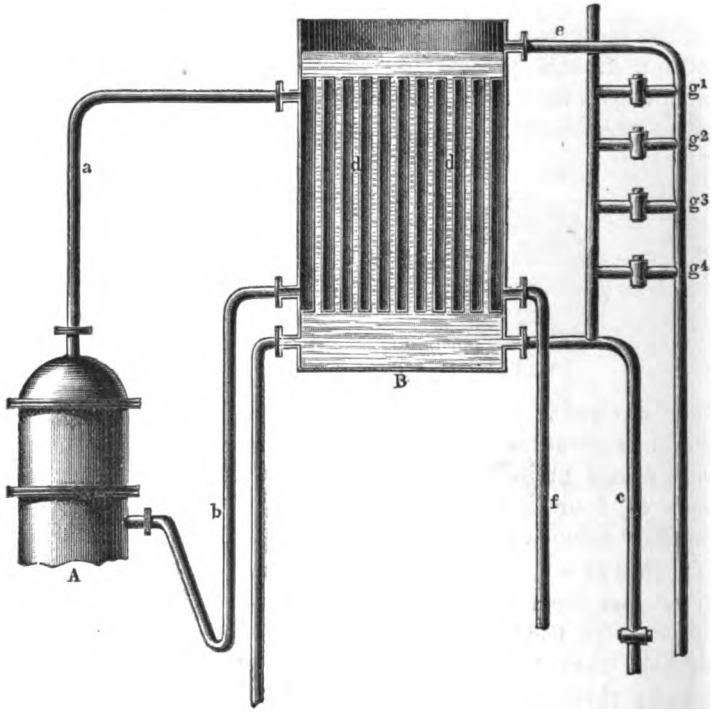
Fig. 121.



The "analyzer" of Coupier's apparatus (G G, fig. 118) would no doubt be advantageously replaced by a more efficient apparatus. This is aimed at in Vedlé's still, where the "benzene rectifier" consists of four larger copper cylinders, surrounded by water, while the "toluene rectifier" resembles that shown in our figure 115 (p. 450) at *n o*, and will be best understood from fig. 122. The vapours pass from the still-head (rectifying-column) A into the analyzer B (6 feet × 2 feet) by the pipe *a*, and the condensed liquid back into A by the pipe *b*, while the uncondensed vapours pass away through *f* into an ordinary worm or condenser of any other form. The vessel B is separated into three parts by two partitions, connected by 60 copper tubes, *d d*, 1¼ inch wide. Water flows through *c* into the lower part of B, thence through *dd* into the upper part and away through *e*. When very little condensate is obtained through *f*, the supply of water through *c* is stopped, and the contents of B are allowed to reach the boiling-point by the heat of the vapours coming from A. At this stage mostly toluene passes over. When this also ceases to flow, the level of water in B is lowered by successively opening the taps g^1 g^2 g^3 g^4, so that ultimately the space in B is altogether filled with steam inside, and with vapours of hydrocarbons outside the tubes *d d*. At this stage almost pure xylene passes over.

Egrot's apparatus (mentioned by Hohenhausen *) is not essentially different from Coupier's.

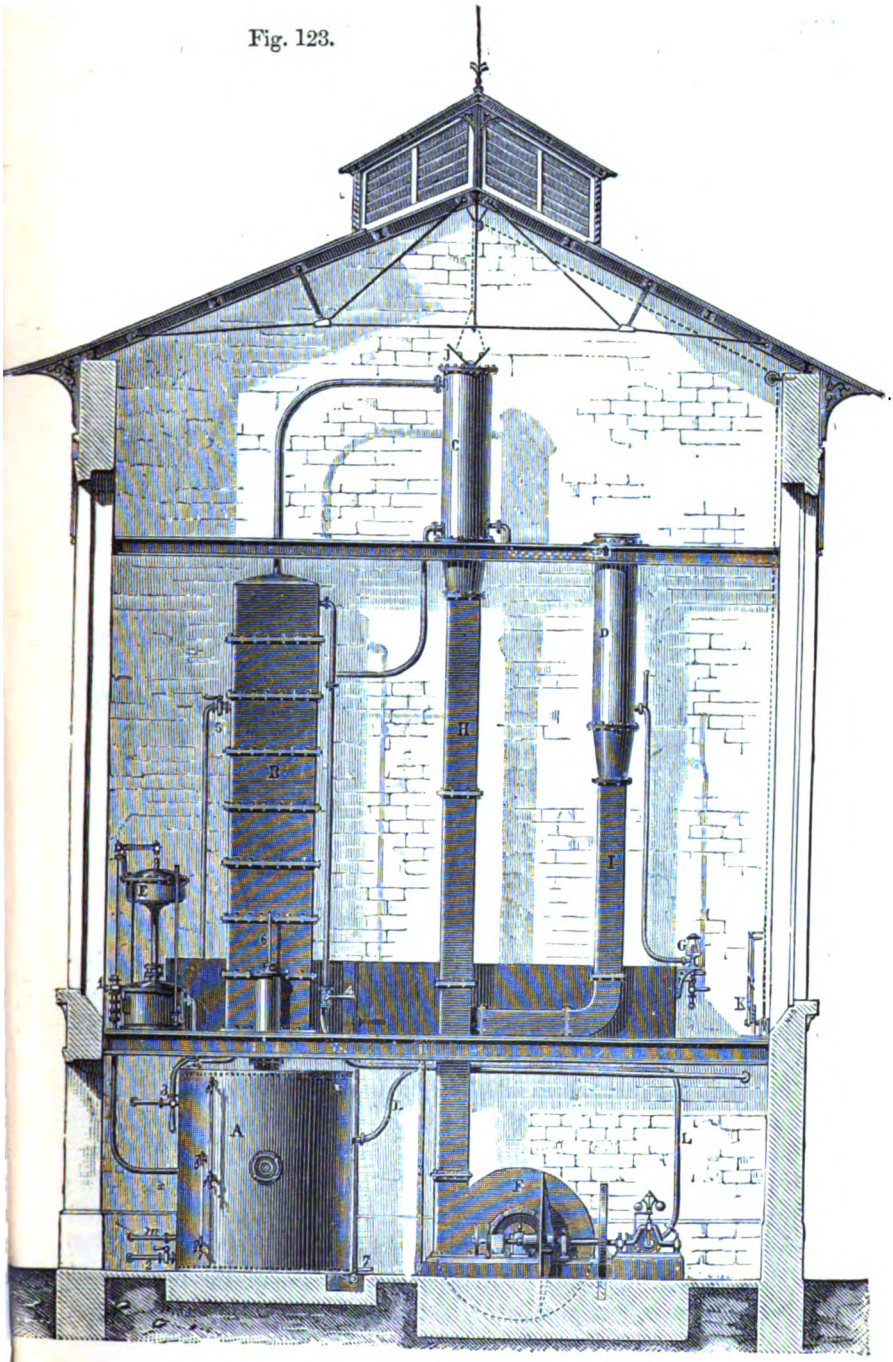
Fig. 122.



The rectifying-apparatus of D. Savalle, fils, of Paris, enjoy special reputation for applicability to the hydrocarbons of coal-tar, and are largely employed by German tar-distillers even for 90- or 50-per-cent benzol. Figs. 123–127 represent this apparatus. In fig. 123, A is the still, heated by a steam-coil; B, a square column for the first condensation; C, the air-condenser for the second condensation of the higher-boiling hydrocarbons which are not passed over into the distillate; D, the air-cooler, in which the distillate itself is condensed. The air is supplied by the fan-blast F, through H to C, and through I to D. J is the slide which

* Journ. Soc. Chem. Ind. 1884, p. 76.

Fig. 123.



regulates the current of air in the condenser, by means of a chain and a graduated lever K. The liquid condensing in D passes through the check-apparatus G for controlling the speed of the distillation. E is a regulator for maintaining a constant pressure

Fig. 124.

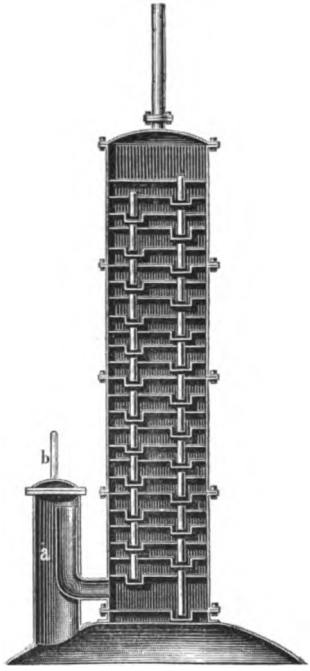
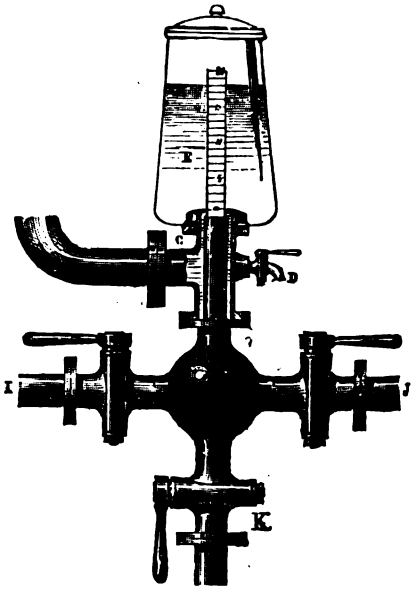


Fig. 125.

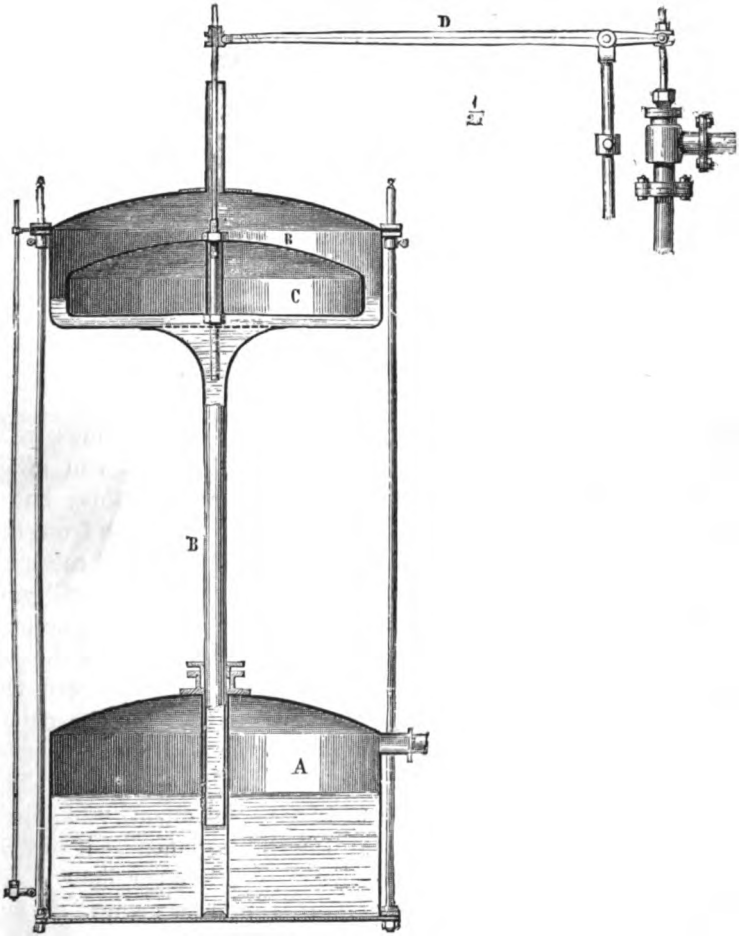


in the apparatus throughout the distillation, L is the steam-engine supplying the fan-blast; 1, steam-valve of the regulator; 2, condensed-water ejector; 3, backflow-tap of the column; 4, purifying-tap of the same; 5, discharge-cock of the upper part of the column; 6, thermometer; 7, tap for discharging and charging the still.

The inner arrangement of the column is shown in fig. 124. The vapours enter it by the cylinder *a*, divided by a vertical partition into compartments, and provided with a thermometer, *b*. The column is divided into several chambers by horizontal perforated partitions. Each partition contains a perpendicular overflow-pipe which partially dips into a corresponding recess of the next lower plate; these overflow-pipes are placed alternately on opposite sides.

The higher-boiling products, flowing down the condenser, thus successively pass through all the chambers and ultimately go back into the column. The perforations of the plates are made of such diameter that the rising current of vapours prevents the liquid from

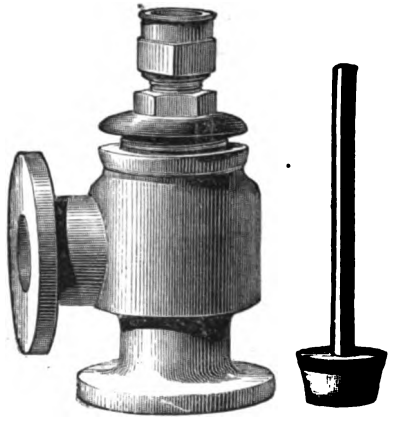
Fig. 126.



falling through them, and a depth of about 2 inches of liquid (corresponding to the top of the overflow-pipes) always remains on the partitions: thus the vapours must always pass through the liquid, which considerably promotes the condensation of the higher-boiling products.

Fig. 125 shows the check-apparatus. The distillate from the cooler passes first into the annular space between the pipes C and F. The upper, graduated portion of the latter projects into the glass jar E, and has a small orifice at F. The space between C and

Fig. 127.



F communicates with E. If the flow of the distillate is such that, with the pressure existing in the apparatus, it can run away through the orifice F, the liquid will not rise above this; but if the speed of flow is in excess of that, the liquid will rise from the annular space between C and F into the jar E. This will cause an hydraulic pressure, in consequence of which the distillate will pass more quickly through F. Thus a state of equilibrium will be produced; and it will be seen that the level of the liquid in the jar E, which can be read off on the graduation of F, depends upon the speed of flow of the distillate. Hence, conversely, the latter may be inferred from the former. The size of the orifice in F must of course be regulated once for all on starting the apparatus. The graduation on F is arranged so as to give the quantity of liquid passing hourly through the apparatus; and a glance at it suffices to show whether the proper quantity of distillate per hour is delivered—that is, whether the apparatus is in order or not. D is a tap for taking samples.

Fig. 126 shows the arrangement of the pressure-regulator. It consists of two superposed vessels connected by a pipe B. The lower vessel, A, is partly filled with water, and communicates through F with the rectifying-column. The upper vessel is pro-

vided with a float C, acting by the lever D upon the conical valve in E. The latter communicates both with the steam-boiler and with the steam-coil heating the still. As soon as pressure is produced in the apparatus, the water must rise in the pipe B, and, when the pressure has attained a certain degree, will enter the upper vessel and lift the float C. This depresses the valve E and checks the supply of steam. If by some accident, as choking up, the pressure in the still should rise too high, the regulator will shut off the steam entirely. By suitable adjustment it can be managed so that, in consequence of the action of the regulator, a certain pressure is never exceeded, which is important both for obtaining a constant product and for preventing accident.

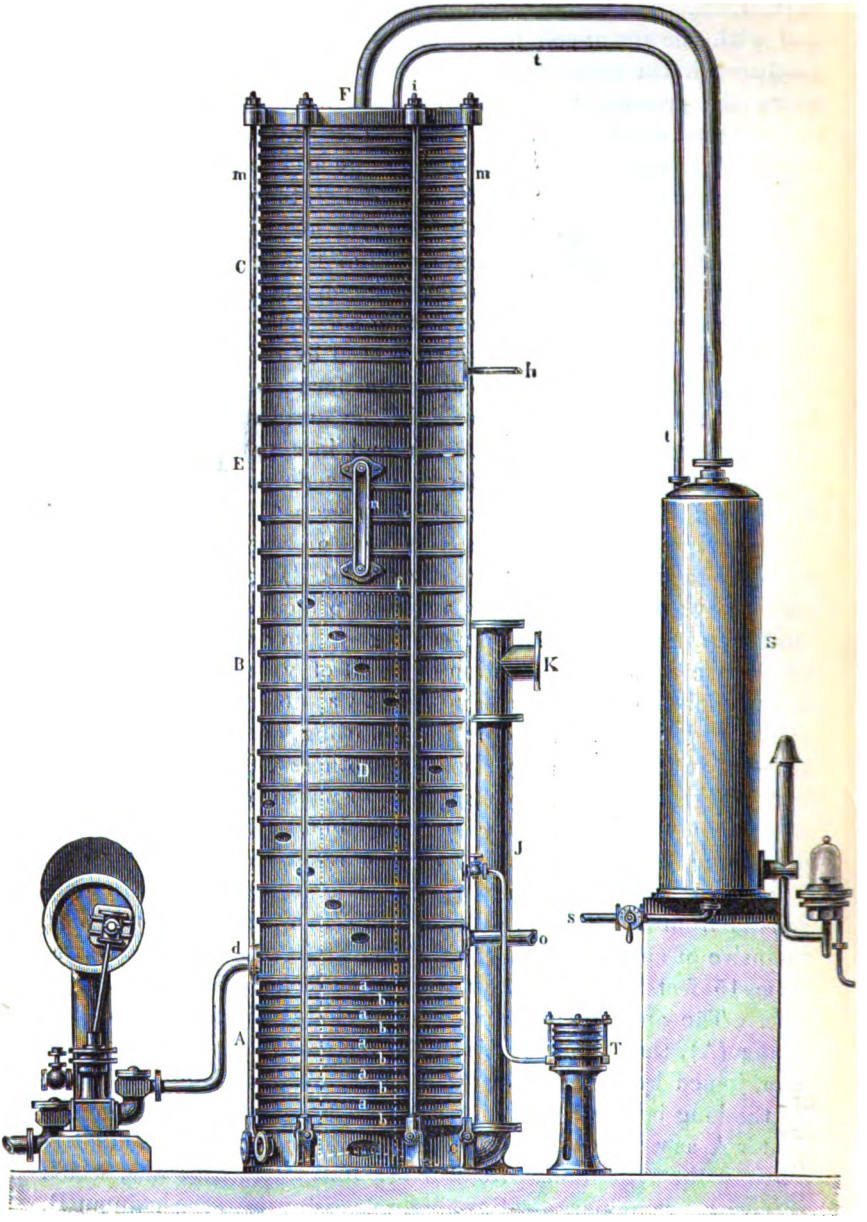
Fig. 127 shows the steam-valve, moved by the regulator.

Further details on Savalle's apparatus for rectifying spirit will be found in the Bulletin de la Société d'Encouragement, 1876, p. 657 (Dingler's Journal, ccxxiii. p. 615), and in a pamphlet by Désiré Savalle, 'Appareils et procédés nouveaux de distillation' (Paris, G. Masson, 1876, 223 pages and 48 diagrams).

The original Savalle apparatus is made of copper; but for benzol cast-iron apparatus are frequently employed, and some manufacturers have such apparatus on a similar principle to, but not identical with, Savalle's. The air-cooling system originally employed by Savalle for the rectification of spirit of wine has been everywhere replaced by water-cooling, as it was not efficient.

The apparatus described in the following, and shown in figures 128–131, was patented (by Siemens Brothers & Co., of Charlottenburg) originally for rectifying spirit (for which purpose 67 of them were already in use in February 1881), but, with a few slight modifications, is equally adapted for the rectifying of coal-tar oils. They construct 13 different sizes of the apparatus, for hourly outputs of from 200 to 1000 gallons, at a cost of from £200 to £550, inclusive of auxiliary apparatus. The height of the column varies from 15 feet in the smallest to 37 feet 6 inches in the largest size. The apparatus is composed of three principal parts—the heater (A), the column (B), and the rectifier (C), all made of cast iron, joined by varnished pasteboard packing and bound together by the long bolts *m m*. In actual work the chambers, *b b*, of the heater A, as well as part of *c*, are full of hot residues; the chambers *a a* and the remaining part of *c* are filled with cold oils, which receive a preliminary heating, before passing into the column B,

Fig. 128.



from being surrounded by the hot residues. The oil is pumped into the heater at *d*, travels round the central tube D in the annular passages *a a*, descends into *c*, passes a portion of this vessel, enters the central tube D by a wide opening, rises up in D, and at *f* enters into the column B. This column consists of a number

Fig. 129.

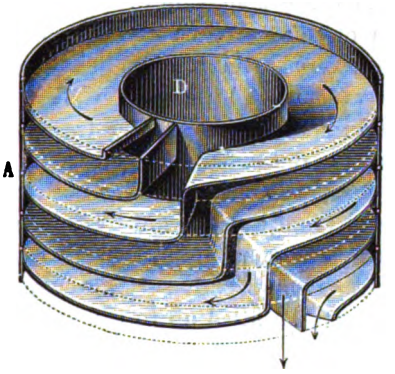
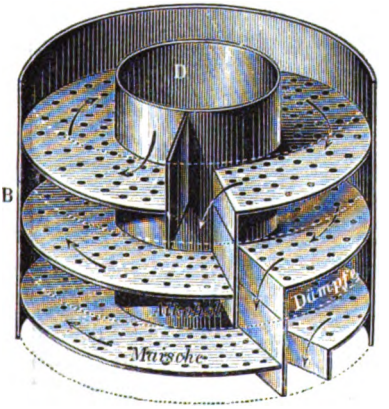


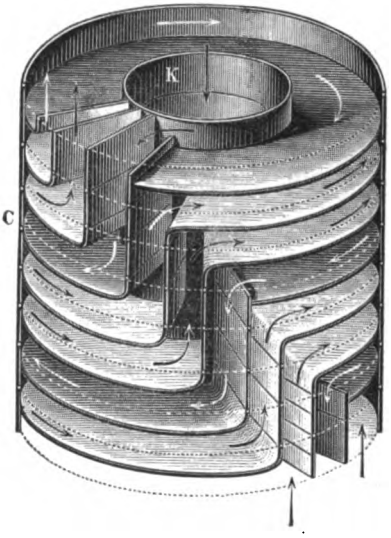
Fig. 130.



of chambers with a central tube open at top and bottom, and a perforated annular bottom. The space below the bottom receives the vapours rising from the liquid underneath; the space above receives the liquid to be rectified. The liquid can only circulate by travelling in one direction round the central tube—but not

quite round, a partition preventing this, whilst a lower opening gives communication with the liquid contained in the next lower chamber. During this passage the oils, circulating in the shape of a long ribbon, lose in the lowest part their more volatile matters by the heat of the steam acting in the copper coil *o*; but the same heat is always used over again for rectifying the contents of an upper portion of the stream, none of these portions getting mixed up together. Thus the evaporation of the more volatile matters takes place with a close approximation to completeness, and with the expenditure of very little steam. The residue, deprived of benzene &c., passes from the lower part of B into the heater, and in the chambers *b b* imparts its heat to a fresh quantity of oils in *a a*; ultimately it runs out continuously through the pipe J at K. The chambers *a a* and *b b* have sloping bottoms; both residues and fresh oils travel from the top downwards, so that no deposit can be formed (which is more important in distilling fermented wort than tar-oils). The space E serves for receiving any froth. The apparatus ought to be filled up to the liquor-gauge *n*.

Fig. 131.



The vapours from B pass into the rectifier, C, composed of a number of chambers in which the vapours are partially cooled by

the surrounding water; the portion which is not liquefied passes at F into the condenser S, whilst the liquefied part collects at the bottoms of the chambers, and, so far as it is not evaporated again, ultimately flows back through an interior pipe into the column B. The cooling-water enters the rectifier at *i*, slowly circulates in it, and runs off hot at *h*. It is expedient to let the water first act in the condenser S, which it enters at *s*, and leaves at *t*, to enter the rectifier at *i*. The check test at T permits the control of the rectification whilst proceeding.

It is asserted that these apparatus require a minimum of steam and of cold water for complete volatilization of the lightest oils, that they are most easily managed, and combine comparatively small first cost with great durability, the material being cast iron.

Fig. 128 is an external elevation; fig. 129, an enlarged section of the heater; fig. 130, a similar section of the column B; fig. 131, a section of the rectifier.

Specially purified benzol is made at some large tar-works by washing the once-rectified benzol over again with sulphuric acid, and passing it once more through the Savalle column or similar rectifying-apparatus. It should now distil within 0°·3, and should not be at all coloured by agitating with sulphuric acid.

Almost *pure benzene* is now found in the trade, sometimes by the name of *benzol for blue*. It distils within half a degree Centigrade, and in the cold solidifies to a white crystalline mass. Even this article contains more or less "neutral oils," *i. e.* such as cannot be nitrified (fatty hydrocarbons) and a little thiophen, as shown by the isatin reaction (p. 118).

Chemically pure benzene, as understood in trade, is sometimes made from the article boiling between 80° and 82°, by allowing it to crystallize in a freezing-mixture, and separating the crystals from the mother liquor by pressing, or by a centrifugal machine. This operation ought to be repeated once or twice. Even then the benzene will contain thiophen; in order to remove this, the benzene must be agitated with renewed quantities of strong sulphuric acid till it ceases to give the blue reaction with isatin.

Practically *pure toluene* and a mixture of the three isomeric *xylenes* are also found in trade.

According to a private communication from Mr. Häussermann, commercial 50-per-cent. benzol sometimes contains up to 0·1 per cent. of pyridine, and the toluene made from it then will contain 0·25 per cent. pyridine. The process for testing for it will be mentioned below.

Nearly pure metaxylene, which is sometimes required for technical purposes, can be made by the following process, communicated to me by Dr. C. Häussermann. Ordinary xylol, which contains but little orthoxylene, is first agitated with 5 per cent. of its weight of strong sulphuric acid, in order to remove the thio-compounds, and is then converted into sulphonic acids by agitating with its own weight of sulphuric acid, sp. gr. 1·84, for several hours. The acid solution is separated from the undissolved portion, and is then treated with a current of steam (as indicated by Armstrong for decomposing sulphonic acids). The metaxylene distilling over needs only to be freed from acid, in order to be worked up at once for metaxylidine. All these operations can be carried out on the manufacturing scale without any difficulty.

Commercial Descriptions of Benzol and Naphtha.

The usual descriptions of the products from light tar-oils yield the following distillates (in percentages by volume), according to my own tests:—

Commercial products.	Initial boiling-point.	88°	93°	100°	110°	120°	130°	138°	149°	160°	171°
	°										
90-per-cent. benzol	82	30	65	90							
50-per-cent. benzol	88	...	13	54	74	90					
Toluol	100	...	...	...	56	90					
Carburetting-naphtha ...	108	...	...	...	1	35	71	84	97		
Solvent naphtha	110	...	...	...	...	17	57	71	90		
Burning-naphtha	138	...	...	...	...	...	...	...	30	71·5	89

The temperatures were all measured with the thermometer-bulb just submerged in the liquid, at the beginning of the distillation.

Häussermann* quotes the following results:—

* Industrie der Theerfarbstoffe, pp. 13 & 14.

At.....	85°	90°	95°	100°	105°	115°	120°	135°	140°	145°	150°	170°	180°
90-per-cent. benzol	20	72	84	95	95	98							
50-per-cent. benzol	...	5	30	50	64	81	94						
Solvent naphtha ...	...	...	...	...	...	...	...	6	48	72	85	92	95

According to another statement, made to me by an English tar-distiller, the ordinary results are :—

At.....	100°	120°	130°	160°	Sp. gr.
90-per-cent. benzol	90	.....	.....	.....	0·885
50-per cent. benzol	50	90	.....	.....	0·880
30-per-cent. benzol	30	90	.....	.....	0·875
Solvent naphtha	.....	.....	20	90	0·875
Burning-naphtha	.....	.....	.....	30	0·885

Hohenhausen quotes :—

Benzol.					
90-per-cent. sp. gr. 0·882.		50-per-cent. sp. gr. 0·878.		30-per-cent. sp. gr. 0·875.	
At °	per cent.	At °	per cent.	At °	per cent.
83	5	94	10	97	12
85	22	95	18	98	21
88	62	98	40	100	30
90	74	100	50	105	55
92	81	105	68	110	73
95	87	110	79	115	84
100	90	115	85	120	90
105	94	120	90		
110	98				

Schultz (comp. also his results, p. 478) quotes :—

At.....	85°	90°	95°	100°	105°	110°	115°	120°
90-per-cent. benzol ...	25	70	83	90	94	97	98	99
50-per-cent. benzol ...	0	4	26	50	62	71	82	90
30-per-cent. benzol ...	0	2	12	30	42	70	82	90

The following statements give the yield of *pure hydrocarbons* from commercial products.

G. E. Davis* finds in 90-per-cent. and 50/90 per cent. benzol:—

	90-per-cent.	50/90 per cent.
Pure benzene	75	50
„ toluene	24	40
„ xylene	1	10

Schultz quotes the following yields, as obtained by a rectifying-column:—

	From 50-per-cent. benzol.	From 90-per-cent. benzol.
Fore-runnings up to 81°...	5 to 10	10 to 17
Pure benzene	30 „ 40	65 „ 75
Benzol for red	5	10
Pure toluene	35 „ 40	2 „ 4
Xylenes	5 „ 8	

Häussermann (private communication) regularly obtains 70 parts of pure benzene from 100 parts of 90-per-cent., and 45 to 48 pure benzene from 100 parts of 50-per-cent. benzene by means of a Savalle's column.

Compare also Coupier's results, p. 464.

Allen† gives the following results of distilling the commercial products in the usual way:—

	Very good first runnings (once-run naphtha).	Good 90-per-cent. benzol.	Scotch 90-per-cent. benzol.	50/90-per-cent. benzol.	30-per-cent. benzol.	Solvent naphtha.	Mixture of 70 pure benzene and 30 toluene.
Spec. grav.	.....	0·882	0·873	0·880	0·875	0·877	0·880
	°	°	°	°	°	°	°
First drop collected at...	.....	82	.....	.....	.....	.....	85·4
10 per cent. „ „ ...	96	83½	84½	94	97	128½	86·6
20 „ „ „ ...	99½	84½	85	95	98	130	87·2
30 „ „ „ ...	102	85	85½	96½	99½	132½	87·8
40 „ „ „ ...	107	85½	86½	98	101	135	88·8
50 „ „ „ ...	111	86½	87½	100	104	137	89·8
60 „ „ „ ...	119	88	89	102½	106	140	91·4
70 „ „ „ ...	128	89½	91½	106	109½	143½	93·2
80 „ „ „ ...	145	92½	94½	110½	113½	148½	96·2
90 „ „ „ ...	170	.....	.....	120	120	156	102·6
92 „ „ „ ...	.....	100					
95 „ „ „ ...	.....	.....	.....	.....	.....	.....	107·0

* Journ. Soc. Chem. Ind. 1885, p. 648.

† Commercial Organic Analysis, 1st ed. vol. ii. p. 87.

According to the same author a good sample of *90-per-cent. benzol* should not begin to distil under 80° and should not yield more than 20 to 30 per cent. at 85°, or much more than 90 per cent. at 100°. An excessive distillate, *e. g.* 35 to 40 per cent. at 85°, indicates a larger proportion of carbon bisulphide (see below) or light hydrocarbons than is desirable. The actual percentage composition of a 90-per-cent. benzol of good quality is about 70 per cent. of benzene, 24 of toluene, a trace of xylene, and 4 to 6 of carbon bisulphide and light hydrocarbons. It should be colourless and free from opalescence. The specific gravity of English 90-per-cent. benzols usually ranges from 0·880 to 0·888 at 15°·5; that of Scotch benzols (which contain little carbon bisulphide, but a considerable proportion of light hydrocarbons) is often as low as 0·871. *50/90-per-cent. benzol* is a product of which 50 per cent. by volume distils over at a temperature not exceeding 100°, and 40 per cent. more below 120°. *30-per-cent. benzol* yields 30 per cent. at 100°, and 60 per cent. more between 100° and 120°; it consists chiefly of toluene and xylene. *Solvent naphtha* gives from 8 to 30 per cent. distillate below 130°, and about 90 below 160°; it consists chiefly of toluene and xylene, with notable quantities of cumene and still higher homologues, and several per cent. of naphthalene [to some of this I must demur; there must be very little toluene in this product; and "cumene" does not occur in coal-tar at all, but only isomers of this body].

Hohenhausen quotes as usual *specific gravities* of English 30-per-cent. benzol 0·875 at 15°, of 50-per-cent. benzol 0·878, of 90-per-cent. benzol 0·882. When the specific gravity is lower than 0·875, the presence of paraffin or non-nitrifiable hydrocarbons may be suspected. Most of the Scotch benzol has a lower specific gravity, on the average 0·870, and contains 7 or 8 per cent. of paraffins, some of it as low as 0·860 (Trewby).

According to Chateau*, in France (1864) the following three classes of benzol were distinguished:—

(*a*) *Very light benzol*, boiling between 80° and 100°. 3 or 4 cubic centimetres of this, added to 5 or 6 c. c. of concentrated oil of vitriol, colour it yellow in the cold without shaking; on being shaken, it first turns orange, then red; the benzol itself

* Bullet. de la Société Industr. de Mulhouse, 1864, p. 97.

remains colourless. On heating, the acid turns much darker, and the benzol turns first yellow, then orange. If the mixture be poured into 10 times its bulk of water and the whole shaken up, a dirty-pink liquid is observed. On standing, a yellow, somewhat muddy, liquid separates.

(*b*) *Light benzol*, distilling between 100° and 120°. In the cold the acid is turned yellow, and on shaking passes through orange into dark red; the benzol first golden yellow, then orange-red. On the addition of water a greenish-yellow muddy liquid is produced; the benzol settling from it is coloured similarly, but lighter.

(*c*) *Heavy benzol*, distilling between 120° and 140°. In the cold the acid turns green, and on shaking passes into blood-red; the benzol is colourless. On heating, the acid turns darker, the benzol yellow, then orange, at last dark red like the acid. On addition of water a dirty grey-green liquid is produced; the liquid floating above is yellow.

These reactions do not seem to possess much practical value for distinguishing the different qualities of benzol; but in any case purified benzol, shaken with strong sulphuric acid, ought to take either a very slight or no coloration.

According to Allen* some contract-notes for continental customers specify the following tests for commercial benzol:—1st, 1 c. c. is agitated with 20 c. c. of pure concentrated sulphuric acid and allowed to stand for some hours. The coloration at the end of this time should be very slight, never exceeding a pale straw-yellow. 2nd, 10 c. c. of the sample is agitated in a stoppered bottle with successive small quantities of saturated bromine-water, until a yellow tint is obtained which remains for some minutes. Not more than 0·5 c. c. of bromine-water should be required to produce this result.

Pure toluene of commerce, according to a private communication from Dr. Häussermann, ought to satisfy the following tests. It ought to boil within 1°. When shaken up for some time with its own volume of strong sulphuric acid, it ought not to cause any coloration. On shaking up for some minutes 90 c. c. of toluene with 10 c. c. of nitric acid of sp. gr. 1·44 in a stoppered jar, the acid ought to assume only a red colour, and to remain quite clear and bright, not to turn greenish or blackish and thick. Some

* Comm. Org. Anal. 2nd ed. ii. p. 475.

samples of toluene which answer to these tests still contain 0·5 per cent. of non-nitrifiable hydrocarbons, which may be troublesome on the large scale; these should be tested for as will be described hereafter, but not less than 1 kilogram of toluene ought to be employed for this test. According to Witt (Chem. Industrie, 1887, p. 9) these impurities can be removed from toluene by agitation with hot sulphuric acid mixed with a little nitric acid, which destroys the thiophens and polymerizes the olefins; the paraffins are not changed, but are easily removed after nitrification by blowing in steam. Toluene (and xylene) purified in this way is stated to yield much more "aniline oil" in the ordinary course of manufacture.

A substance occurring only in the strongest benzol, to which attention has recently been drawn, is *carbon bisulphide*. This body has been indicated, amongst others, by Vincent and Delachanal*. Watson Smith (private comm.) has observed in English benzols up to 5 per cent. carbon bisulphide, which gave rise to complaints. The occurrence of this substance is easily accounted for, all conditions for its formation being present in the gas-retorts, viz. red-hot carbon and vapour of sulphur (from the pyrites which always occurs in coal); neither do the ordinary purifying agents, viz. sulphuric acid and alkali, remove it. It is true that a good deal of the carbon bisulphide existing in raw tar will remain uncondensed during the distillation; but some of it must pass into the lightest oils, and more will pass the more perfect the condensing-plant is. Its smell does not betray it, even when 20 per cent. is mixed with benzol, which is much in excess of any thing ever occurring in practice. 5 per cent. CS_2 in benzol makes no difference whatever in the smell; and even the first distillate smells of benzene, not of CS_2. But a safe test is afforded by the specific gravity, which is much raised by CS_2. Watson Smith, on adding 5 parts of CS_2 to 100 of benzol of sp. gr. 0·875, yielding 20 per cent. below 100°, got on distilling 35 per cent. below 100°, of sp. gr. 0·917. By employing a Linnemann's fractionating apparatus or the like, probably nearly pure CS_2 would have been got out. On the large scale, benzol refiners now separate the first portions of the distillate as "fore-runnings" ("Vorlauf"). These contain, along with some benzene, the just-described impurities, along with acetone, methylic cyanide, and other substances not yet fully investigated.

* Compt. Rend. lxxxvi. p. 340.

Apart from the specific gravity, the presence of CS_2 can be detected by alcoholic potash, which forms crystals of potassium xanthate (see below), or by alcoholic ammonia, which forms ammonium sulphocyanide, easily recognizable by the blood-red reaction with ferric chloride. J. B. Cohen* has tried to apply Traube's capillarometer (devised for estimating fusel-oil in spirits of wine) to discovering carbon bisulphide, as well as fatty hydrocarbons, in benzol. His own paper shows that that reaction can hardly as yet lay claim to more than a qualitative value. We shall describe the quantitative tests for CS_2 lower down.

Pyridine and other basic substances are detected by agitating 100 parts of benzol with 4 parts of 10-per-cent. sulphuric acid for half an hour, separating the acid solution by means of a tap-funnel, making it alkaline with caustic soda, and distilling in a current of steam. The distillate is saturated with nitric acid and evaporated to dryness on a water-bath. Or else, in lieu of distilling, the free bases are extracted from the solution by means of ether. Properly purified benzol ought not to contain anything soluble in dilute sulphuric acid, and but little imparting a dark colour to strong sulphuric acid. Sometimes a maximum is stipulated for the percentage of substances dissolved out by strong sulphuric acid, viz. non-saturated hydrocarbons and thiophens. The former can also be determined by titration with bromine-water. Nitric acid of sp. gr. 1·4 ought not to produce any white vapours when poured into benzol, and ought not to colour the benzol on agitating.

The *fatty hydrocarbons* contained in benzol belong to the series C_nH_{2n+2}, C_nH_{2n}, and C_nH_{2n-2}; there are, moreover, present methyl cyanide, isocyanides, thiophen and its isomers; perhaps, but at all events quite exceptionally, ethylic alcohol (p. 137).

To distinguish coal-tar benzol or naphtha from petroleum or shale-spirit &c., which are also frequently called "benzolene, naphtha," &c., and which may easily occur as adulterations of the former, is not difficult. Both products can be at once distinguished by their smell, if unmixed; but in mixtures the smell of coal-naphtha prevails over even a very large addition of petroleum or shale-spirit. But the specific gravity affords a good test: with coal-naphtha it is always above 0·870 at 15°, with petroleum spirit &c. below or at most very little above 0·700. There is, however, the drawback that carbon bisulphide *raises* the density of benzol, so that it would compensate a lowering produced by petroleum

* Chemical News, liv. p. 306.

hydrocarbons. Very distinct is the reaction with nitric acid, which at once acts upon the aromatic hydrocarbons of coal-tar, but hardly at all upon the fatty compounds of petroleum or paraffin oil.

The following useful synopsis of the characters of the two kinds of products has been made by A. Allen*:—

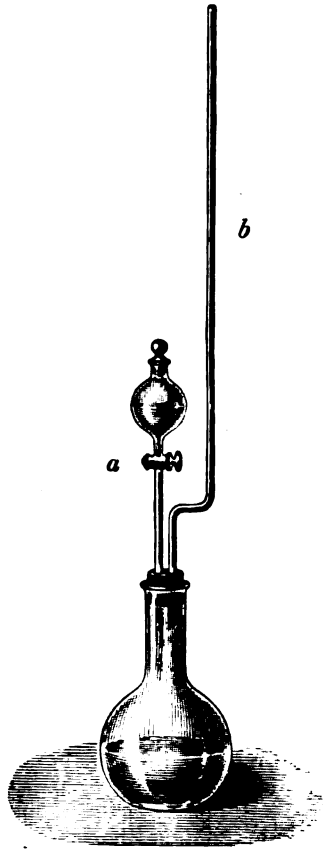
Petroleum spirit, Benzoline, Benzene.	*Coal-tar Naphtha, or "Benzol."*
1. Consists of heptane (C_7H_{16}) and its homologues.	1. Consists of benzene (C_6H_6) and its homologues.
2. Heptane contains 84·0 per cent. of carbon.	2. Benzene contains 92·3 per cent. of carbon.
3. Commences to boil at 54–60° C.	3. Commences to boil at about 80° C.
4. Specific gravity at 15°·5 about 0·69 to 0·72.	4. Specific gravity about 0·880.
5. Smells of petroleum.	5. Smells of coal-tar.
6. Dissolves iodine, forming a solution of a raspberry-red colour.	6. Dissolves iodine, forming a purple-red liquid of the tint of an aqueous solution of potassium permanganate.
7. Does not sensibly dissolve coal-tar pitch, and is scarcely coloured by it even on prolonged contact.	7. Readily dissolves coal-tar pitch, forming a deep-brown solution.
8. When shaken cold with one third of its volume of fused crystals of absolute carbolic acid, the latter remains undissolved and forms a separate lower stratum.	8. Miscible with absolute carbolic acid in all proportions.
9. Requires two volumes of absolute alcohol, or 4 or 5 volumes of methylated spirit of sp. gr. 0·828, for complete solution at the ordinary temperature.	9. Miscible with absolute alcohol in all proportions. Forms a homogeneous liquid with an equal measure of methylated spirit of sp. gr. 0·828.
10. Warmed with four measures of nitric acid of sp. gr. 1·45, the acid is coloured brown, but the spirit is little acted on and forms an upper layer.	10. Completely miscible with four measures of nitric acid of sp. gr. 1·45, with great rise of temperature and production of dark-brown colour. A portion of the nitrobenzene produced may separate out as the liquid cools.

No. 10 is capable of giving quantitative results in separating the two kinds of oil. The oil to be tested is treated with nitric acid of sp. gr. 1·45 in a small flask with an inverted condenser. When action has nearly ceased, the whole is poured into a narrow graduated tube; the measure of the upper layer indicates approximately the amount of petroleum spirit present. If the proportion of benzene is considerable, the nitrobenzene formed may not remain completely dissolved in the acid, but form a layer of dark-brown colour below the stratum of petroleum spirit. Nitrobenzene and petroleum spirit are readily miscible in the absence of nitric acid; but agitation with strong nitric acid dissolves out the nitrobenzene, a portion of which may rise and form an intermediate layer as above described.

* Chemical News, xl. p. 101.

Even when a fraudulent admixture of petroleum spirit &c. is out of the question, the *nitrification test* should be applied, since more or less non-nitrifiable hydrocarbons are generally contained in the tar, especially owing to the admixture of tar from cannel coal, bituminous shale, &c. This test gives an idea of how much nitrobenzene may be expected on the large scale. Place 100 c. c. benzene in a flask of about 500 c. c. capacity, provided with a dropping funnel *a* and a long tube *b* (fig. 132) for condensing any hydrocarbon volatilizing. Prepare a mixture of 150 gr. nitric acid of sp. gr. 1·4 and 180 or 200 gr. sulphuric acid sp. gr. 1·84, which must be allowed to cool before use. Run this drop by drop through the tap-funnel *a* into the benzol, shaking this up almost constantly. As soon as the temperature rises, cool the flask by immersing it in a dish full of water. When all the acid has been added, and when no further rise of temperature takes place spontaneously, heat the flask gently for an hour or two (during this time the tube *b* is best replaced by a proper reflux-condenser). Allow the whole to settle, and separate the lower acid layer by means of a separating funnel from the crude nitrobenzene. Dilute the acid with several times its bulk of water; any oily liquid separating after a few hours' rest is added to the nitrobenzene. Wash the crude nitrobenzene three times with its own bulk of water, once with a very dilute solution of caustic soda (if this solution is employed too concentrated, an emulsion is formed which is very awkward to manage), and once more with water, taking care that no oil is lost in separating the washings. The well-settled liquor can be at once tested for its specific gravity, which, in the case of 90-per-cent.

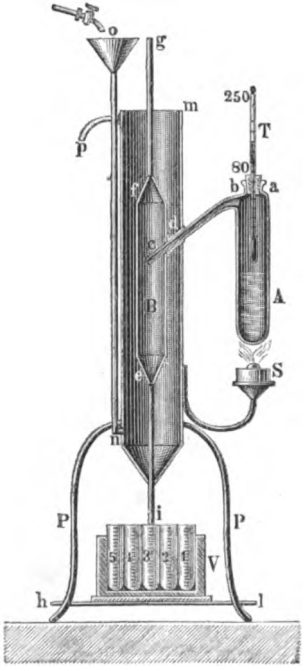
Fig. 132.



benzol, ought to be 1·20, with 50-per-cent. benzol 1·19 at 15°; but this is not decisive, as the nitrobenzol is not quite free from water, and some benzol may have escaped nitrification. The liquor is therefore distilled from a fractionating-flask (fig. 110, p. 432), till the temperature has reached 150°, and the distillate is once more nitrated, but this time with a large excess of the acid mixture; anything remaining undissolved may be considered as non-nitrifiable hydrocarbons. Theoretically 100 parts of benzene furnish 157·6 of nitrobenzene, 100 parts of toluene: 148·9 of nitrotoluene.

For testing benzol by fractional distillation, usually ordinary glass retorts or fractionating-bulbs are employed, as fig. 110, p. 432. In this case the position of the thermometer is of great importance (p. 430), and also in other respects different results may be

Fig. 133.

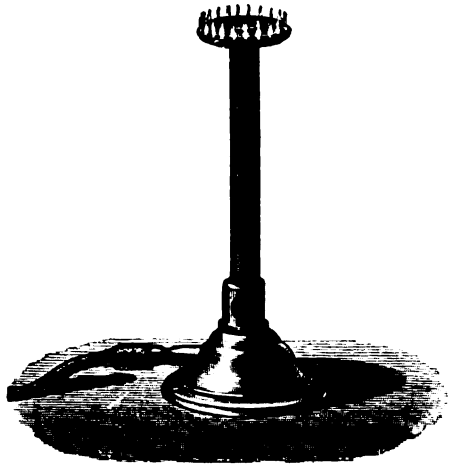


obtained in apparatus of unequal construction. On this account, and on account of the fragile nature of glass retorts, Regnault, at the instance of the French Government, constructed a standard apparatus*, which is shown in section in fig. 133. A is a cylin-

* Ann. Chim. Phys. lxviii. p. 409.

drical copper retort with a neck *a* and a bent vapour-tube *b c*. The latter fits tightly into the lateral tubule *d* of the condenser B. This consists of a brass cylinder *e f*, ending at top and bottom in narrow metal tubes *g* and *i*, and fixed air-tight in a wider metal cylinder *m n*. Into the latter enters a stream of water through *o* at the bottom and leaves at the top at *p*. It stands on a tripod P P, to which a horizontal frame *h l* is attached. In the latter slides a carrier V, containing five glass tubes, closed at the bottom and divided into cubic centimetres, each of which can be thus brought under the outlet-pipe *i* of the condenser. By means of a pipette the retort is charged with 100 c. c. of oil, which ought not to occupy much more than a third of it. The thermometer T is fixed in the tubule *a* so that its bulb does not dip into the liquid, and that the 80th degree comes out very little above the cork. The distillation is carried on by the gas- or alcohol-flame S. The ordinary fixed points for changing the receivers 1 to 5 are 100°, 120°, 140°, 160°, and 180°. The convenience of this arrangement for changing the receivers and reading-off the volume of each fraction will be at once apparent. The condenser is cooled by means of water.

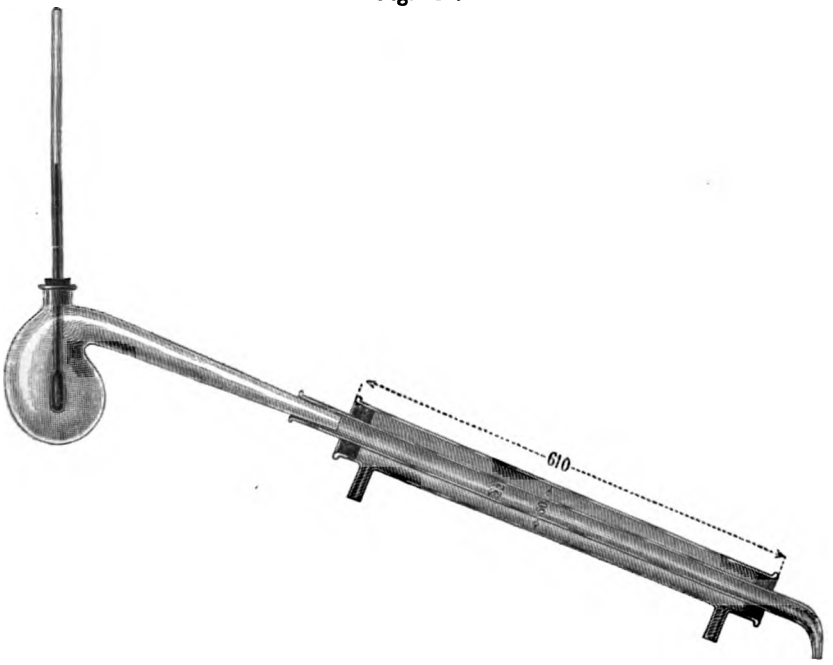
Fig. 134.



At the tar-works and at the buyers' laboratories glass retorts are employed for testing benzol. Frequently differences of opinion occur between buyer and seller, chiefly caused by the fact that it is not usual in the English trade to place the thermometer in the

only proper position, as shown in the diagram fig. 110, p. 432, but to let it dip more or less into the liquid. Further deviations are caused by differences in the size of the retorts and the speed of the distillation. The following detailed directions by W. W. Staveley* are intended to produce a uniform result; but this would involve their being accepted everywhere as binding, which is far from being the case. 100 c. c. of the sample is to be put into an ordinary 6-ounce stoppered retort, connected with a Liebig's condenser whose condensing-tube is 1 inch wide and 30 inches long. The thermometer is so fixed that its lowest point is $\frac{3}{8}$ inch from the lowest portion of the retort. Heat is applied by means of a Bunsen rose-burner (fig. 134), in such a manner that the distillate runs in separate drops into the 100 c. c. burette employed

Fig. 135.



as the receiver. A moment before the desired temperature is reached the lamp is removed, whereupon the thermometer rises to the proper point; and the reading-off is made as soon as the benzol has ceased to drop from the condensing-tube. The contents of the

* Chemical News, xliii. p. 70.

retort, after cooling, are poured into the burette; and the loss, if any, is added to the percentage of the distillate. New corks absorb benzol, and hence are not to be recommended; neither are new clean retorts suitable, unless a few grains of brick are introduced. Best of all are retorts which, having been used for some time, have a slight coating of carbon inside.

In 1886 I found at the largest English tar-works 8-ounce retorts, whose beaks dip into condensing-tubes $\frac{7}{8}$ inch wide and 27 inches long, surrounded by a glass cooler, as shown in fig. 135. The thermometer is so placed in the retort that its end is $\frac{3}{8}$ inch from the bottom.

Allen*, in contradiction to many assertions concerning the uncertain results of the ordinary English commercial-benzol testing, asserts that very constant results can be obtained by different operators, the variations rarely exceeding 1 or $1\frac{1}{2}$ per cent., if the test is properly understood. He gives the following instructions for conducting the ordinary retort-test so as to ensure results as accurate as the process will permit of. They apply to 90-per-cent. benzol, which must, of course, be modified to suit other qualities. 100 c. c. of the benzol is measured in an accurately graduated cylinder, and poured thence into a tubulated retort holding 200 c. c. or 8 fluid ounces. A delicate thermometer, 14 inches long and with a small bulb, is fixed in the tubulure by a cork so as to be vertical, and so that its bottom is $\frac{3}{8}$ inch distant from the bottom of the retort. The first marking or division of the thermometer is at 70°, which point should be well out of the retort, and the graduation should be continued up to 130°, with divisions at each $\frac{1}{2}$, or better $\frac{1}{5}$, of a degree Centigrade. Thermometers, otherwise similar, but differing some 6 inches in the height of the 100° mark, give distinctly different percentages in benzol-testing†. The neck of the retort is inserted into the inner tube of a Liebig's condenser, and pushed as far as it will go. The condenser should be from 15 to 18 inches in length, and well supplied with cold water. The neck of the retort should not project too far into it, and, if necessary, should be cut short. No cork or other connection is necessary between the retort-neck and condenser-tube. Before use, both the retort and the condenser should be rinsed with a little of the sample and allowed to drain; or a little benzol is distilled in it and the residue carefully drained out. The graduated cylinder

* Comm. Org. Analy. 2nd ed. ii. p. 406.

† Proper thermometers are obtainable of L. Casella, 147 Holborn Bars, E.C.

employed for measuring out the sample is next placed (without drying it) under the further end of the condenser-tube in such a manner as to catch all the distillate, while allowing it to drop freely. The retort is then heated by the naked flame of a Bunsen burner, furnished with an air-regulator working automatically with each movement of the tap, and surrounded with a cylinder to exclude currents of air*. The flame should be small, about the size and shape of a filbert, and when the distillation of the benzol commences, must be so regulated that the condensed liquid shall fall rapidly in distinct drops, not in a trickle or a continuous stream.

When the distillation commences, the flame is regulated, if necessary, and the rise of the thermometer carefully watched. The moment it registers 85°, the flame is extinguished. But as the thermometer always rises from ½ to 1 degree, this must be allowed for. A little experience shows the amount of this after-rise for each special case; thus, if it be 1°, the gas should be turned out when the thermometer registers 84°·5, because it will still rise to 85°·5, and thus 85°·0 may be considered the mean reading. Four or five minutes are allowed for the liquid in the condenser to drain into the measuring-cylinder, and then the volume of the distillate is carefully read off and recorded. The lamp is then re-lighted, and the distillation continued till the thermometer rises to 100° (observing the same precaution as to the after-rise), when the gas is turned off as before, and the volume of the distillate is read off, allowing time for drainage. The residual liquid in the retort is allowed to cool, and is then poured, to the last drop, into the measuring-cylinder. A deficiency from the 100 c. c. originally taken will generally be observed. This deficiency, amounting to 1 c. c. or so, which is supposed to be caused by loss of benzol (although it is due far more to expulsion of acetylene and other gases), is added to the reading for each temperature, and the corrected volumes reported as the "strength" of the benzol examined. The variations in barometric pressure are allowed for by deducting or adding 1° C. for each inch below or above 30 inches. Thus, if the barometer marks 29·5 inches, the gas should be so extinguished that the thermometer may mark a mean temperature of 99°·5 instead of 100°. [According to my observations this correction does not hold good for elevated situations, where the deviation from 30 inches is too great; in that case the only

* It is well to place the lamp in a deep tin basin to hold the benzol in the event of a retort cracking.

practicable way is to distil pure benzene at the same time, and regulate the thermometer accordingly, as will be explained below.]

An anonymous writer* has asserted that for each $\frac{1}{10}$ inch lowering of the barometer 0·8 per cent. more is found than at the normal pressure; but this is evidently exaggerated. W. Thomson† recommends immersing the distilling-vessel entirely in a copper water-bath, so that the quantity passing over will be ascertained independently of the shape of the vessel, the state of the barometer, &c.; then the water might be siphoned off, and the copper box used as an air-bath for the higher temperatures. But it is here overlooked that the temperature inside the retort is several degrees below that of the water- or air-bath. In any case the water-bath would have to be brought, by the addition of common salt or the like, to such a temperature as to raise that inside the retort to 100°.

I have myself, in an extended investigation‡, in which I was aided by contributions from many of the largest producers and consumers of benzol, shown the great uncertainty attaching to all the ordinary testing methods founded on fractional distillation. It was found that the results were influenced by the following circumstances:—the material of the retort (glass or metal); the shape of the same; the presence or absence of a dephlegmator; the exact position of the gas-delivery tube with reference to the level of the liquid, its width, and the way it was joined to the neck of the flask; the position of the thermometer; the length, width, and inclination of the condenser; the rate of distillation; the mode of reading-off; the barometric pressure. Uniform results can only be obtained by eliminating most or all of these disturbing influences, preferably in the following manner. A quantity of the purest obtainable article is set aside as the "type." The sample to be tested is distilled in any suitable apparatus, the more rationally constructed the better, and immediately before or after a similar quantity of the "type" is distilled in the same apparatus exactly in the same way.

The above investigations were continued by a special committee of the German Society of Chemical Industry, whose report has been made by Dr. Bannow§. There was an extraordinary diversity of opinions, which ultimately led to the conclusion that different classes of substances, as alcohols, phenols, hydrocarbons,

* Chem. News, xliii. p. 93; li. p. 170.
† Ibid. xliii. p. 115.
‡ Chemische Industrie, 1884, p. 150.
§ Ibid. 1886, p. 328.

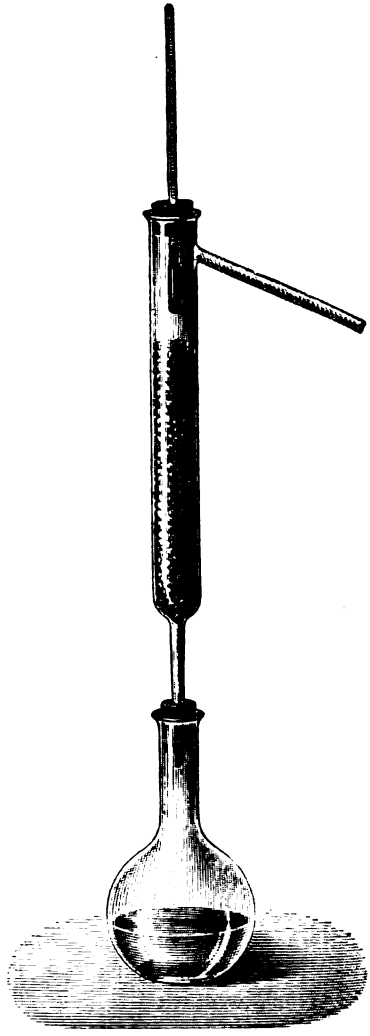
bases, &c., behaved differently with regard to their boiling-points, and that hence uniform rules for determining boiling-points can hardly be established. Bannow himself (the manager of Kahlbaum's works) employs for the most heterogeneous substances a globular retort of a capacity of 200 c. c. (say, 7 ounces), made of platinum, silver, or copper, 0·7 millimetre (= $\frac{1}{36}$ inch) thick, and 73 millimetres (= about 3 inches) diameter, consisting of two flanged halves screwed together and made tight with a ring of wetted or oiled cardboard. On the top there is a neck, 1 inch long and $\frac{3}{4}$ inch wide, provided with a glass still-head, $\frac{1}{2}$ inch wide outside and 4 inches long, with a globular enlargement in the centre, and $\frac{3}{8}$ above this a side tube, branching off nearly at a right angle, sealed on without any contraction. The still rests on asbestos cardboard, with a circular hole of $1\frac{1}{4}$ inch diameter, and is heated by a plain Bunsen burner, whose flame burns always blue. The cooler is 800 millim. (=31 inches) long, and inclined at such an angle that the outlet is 4 inches below the inlet. The thermometer is made of thin glass, not thicker than half the width of the glass still-head; the mercury-bulb is placed in the centre of the globular enlargement. The thermometer-scale can be moved up and down by means of an adjusting-screw. The charge is 110 c. c.; the 3 c. c. first distilling are rejected, and the distillation is carried on so that 5 c. c. per minute, or 2 drops per second, pass over. It is continued till the receiver has been filled up to 100 c. c. No correction is made for barometric pressure; but the thermometer-scale is adjusted by means of the screw before every test, by distilling 100 c. c. of a normal "type," and fixing the scale in the moment when 60 c. c. have passed over.—Most of these points were adopted by the other members of the commission; but they all objected to the use of metal retorts, preferring glass, and to the rejection of the first and last portions of the distillate [which, in point of fact, is not possible in benzol-testing].

Mendelejeff* has employed, for the testing of Caucasian petroleum, a special method, consisting in conducting the vapours issuing from the dephlegmator of the first retort through a tube which passes down to the bottom of the second retort, and from there through a dephlegmator of the same contrivance into a third, fourth, and fifth retort. When the temperature of the last retort has reached the height desired, the distillation is discontinued,

* Journ. Soc. Chem. Ind. 1883, p. 371.

and only resumed after the contents of the first retort have absorbed the contents of the remaining ones. Thus a very great number of fractions were obtained.

Fig. 136.



In order to avoid the influence of *carbon bisulphide* on the testing of benzol, which frequently leads to awkward irregularities (compare the statements of Watson Smith, p. 481), Nickels* treats the benzol twice with 10 per cent. by volume of a hot saturated solution of caustic potash in absolute alcohol, agitates for two hours, filters from the precipitate of potassium xanthate, formed by the reaction

$$CS_2 + KOH + C_2H_6O = H_2O + CS(O.C_2H_5)SK,$$

removes the alcohol from the filtrate by twice washing with its own volume of water, removes the water suspended and dissolved by agitating with a little plaster of Paris, and distils as usual. Thus much more constant results are obtained than without that purification; the benzol now shows a lower specific gravity (0·882 or 0·880, instead of 0·885), and is quite free from alliaceous smell.

If the object of testing benzol is not to conform to an arbitrary commercial standard, but to ascertain its real composition, the common retort or fractionating-bulb ought to be replaced by a more perfect apparatus for fractional distillation, *e. g.* Linnemann's three-bulb tube, fitted with platinum-gauze cups, or a Le Bel-

* Chem. News, xliii. pp. 148, 250.

Henninger three-bulb tube, which is the apparatus most usually employed in England. A Hempel tube, as shown in fig. 136, is quite as efficient and less liable to breakage; it is a simple tube, narrower at the bottom, and with a side-branch near the top, filled with rough glass beads.

The following results were obtained by Mr. B. Nickels from the same benzol (A, when distilled in an 8-oz. retort in the ordinary way; B, after removing the carbon bisulphide in the manner described on p. 492; C, when the *purified* benzol was distilled in a three-bulb apparatus instead of in an 8-oz. retort) :—

	A. Commercial 90-per-cent. benzol in 8-oz. retort.	B. A after being purified from CS_2 in 8-oz. retort.	C. B distilled in flask with three-bulb apparatus.
Spec. grav. at 15°·5 ...	0·884	0·881	0·881
First drop distilled at	79·5	83·4	.....
5 per cent. „ „	.....	84·2	81·25
10 „ „ „	.....	84·3	82·0
20 „ „ „	.....	85·0	82·8
25 „ „ „	84·0	.....	.....
30 „ „ „	85·0	85·8	83·0
40 „ „ „	85·4	86·4	83·5
50 „ „ „	86·4	87·1	84·7
60 „ „ „	88·0	88·3	85·3
70 „ „ „	90·0	90·0	86·5
80 „ „ „	93·0	93·0	89·3
90 „ „ „	100·0	100·0	100·0
95 „ „ „	.....	112·4	111·8

By operating on 300 c. c. of the same sample, removing the carbon bisulphide by alcoholic potash, and several times repeating the process of fractionating with the three-bulb apparatus, Mr. Nickels obtained the following results as indicative of the proximate analysis of the benzol tested :—

	per cent.
Carbon bisulphide	1·5
Light hydrocarbons, sp. gr. 0·872 (not nitrifiable, probably chiefly amylene and acetonitrile)	3·5
Benzene, sp. gr. 0·885, distilling within a range of 2 degrees	78·4
Toluene, sp. gr. 0·8715, distilling within 2 degrees	16·6
	100·0

It is very desirable that the present empirical and conventional mode of benzol-testing should be replaced, at any rate in important cases, by the above scientific treatment.

Special tests for *estimating the quantity of carbon bisulphide* in benzol are the following:—Nickels converts the potassium xanthate, formed in the above-described method for obtaining benzol free from CS_2 (p. 492), into copper xanthate, and weighs the latter. Holland and Phillips* put 2 c. c. of the benzol to be tested into a piece of combustion-tubing about 12 or 13 inches long, sealed at one end and drawn out at the other extremity, so as to form a funnel; they add 5 c. c. of a solution of ferric chloride, containing 240 grams Fe_2Cl_6 in 1000 c. c., and 10 c. c. of strong ammonia. The tube is carefully sealed before a lamp and well shaken; it is then wrapped in a cloth and immersed in boiling water for an hour or so. At the expiration of that time, the tube is taken out, allowed to cool, and opened. The following reaction will have taken place in the first instance:—

$$CS_2 + 4\,NH_5O = NH_4.CNS + (NH_4)_2S + 4\,H_2O,$$

but the presence of ferric chloride will have caused the sulphur of the ammonium sulphide to be converted into FeS. This is now oxidized along with the sulphur of the thiocyanate in the following manner:—The contents of the tube are transferred to a flask holding about ½ litre, and are evaporated, just to dryness, by careful manipulation over a Bunsen flame; 20 c. c. of fuming nitric acid is added, and the whole is boiled nearly to dryness. If any sulphur is left unoxidized, a little more nitric acid must be added. Lastly hydrochloric acid is added and some water; the solution is filtered, and the sulphuric acid in the filtrate is determined in the usual manner as barium sulphate. As it is not possible to get the whole of the ferrous sulphide out of the tube with water alone, this is best done by means of a little hydrochloric acid and a few grains of potassium chlorate.

Holland and Phillips have tested the accuracy of their method by a number of very satisfactory experiments with mixtures of known quantities of CS_2 and absolutely pure benzene, and have thereby obtained from commercial samples the following results:—

* Journ. Soc. Chem. Ind. 1884, p. 206.

CS_2 contained in :—

Ordinary Lancashire tar-benzols :

50-per-cent. benzol ..... (*a*) 1·165 ; (*b*) 0·825 ; (*c*) 0·894 per cent.
90 „ „ „ ..... (*a*) 1·625 ; (*b*) 1·975 ; (*c*) 1·930 per cent.
Toluol ..... (*a*) 0·164 ; (*b*) 0·170 per cent.

Carbonizing benzols (various samples) :

0·178 ; 0·131 ; 0·174 ; 2·450 ; 0·134 ; 0·246 per cent.

Ordinary crude naphthas :

0·143 ; 0·207 per cent.

Specially purified benzols :

50 per cent. = 0·192 ; 90 per cent. = 0·204.

"Pure benzene" from various dealers in chemicals :

0·716 ; 0·551 ; 0·722 ; 0·684 per cent.

They add that their method will return any other sulphur compounds, present in benzol, as carbon bisulphide, but that these bodies are only present in small quantities, and that they are impurities as well.

[Thiophen, according to a private communication from V. Meyer to the author, would *not* be acted upon by the above-described treatment.]

A special method for the testing of commercial *xylol*, in order to determine the quantity of the *three isomeric xylenes and of neutral oils*, has been published by Levinstein*, based on the behaviour of those substances towards nitric acid, concentrated sulphuric acid, and fuming oil of vitriol. This is very important, since the commercial xylol, although boiling within two degrees, contains the three isomers in very different quantity, while only one of them, metaxylene, is of technical importance. The method is as follows :—

A. *Estimation of Metaxylene and Paraffins.*

Heat 100 c. c. of the crude xylol to 100° in a sand-bath, together with dilute nitric acid (40 c. c. acid of spec. grav. 1·40 and 60 c. c. of water), from half an hour to an hour, or until red fumes are no longer evolved, taking care to thoroughly mix the acid with

* Journ. Soc. Chem. Ind. 1884, p. 77 ; compare also Jacobsen, p. 121.

the hydrocarbons; separate the latter from the acid, add to the hydrocarbons an excess of caustic soda, and distil by wet steam. The distillate consists of water and metaxylene, mixed with paraffins. The hydrocarbons are separated from the water, and about $1\frac{1}{2}$ of their volume of concentrated sulphuric acid is added and well mixed for half an hour, when the metaxylene will be dissolved, leaving the paraffins unaltered. Instead of distilling the above mixture, several times washing with caustic soda will also be sufficient; the ortho- and paratoluene have been converted into toluic acids or their nitro-compounds, and are removed by the soda, whilst metaxylene is very little altered by the treatment with dilute nitric acid. The c. c. of metaxylene plus paraffin, and then the c. c. of the latter alone, are read off, and at once indicate percentages.

B. *Estimation of Paraxylene.*

Take 100 c. c. of the crude xylene, agitate with 120 c. c. concentrated sulphuric acid (170° Tw.) for half an hour, cooling the mixture till no more is dissolved, and allow to settle. The residual hydrocarbons, consisting of paraxylene and paraffins, are separated, measured, and heated for a short time on a water-bath with fuming sulphuric acid containing 20 per cent. SO_3; allow to settle, and separate the paraffin, which is again measured.

C. *Estimation of Orthoxylene.*

In ordinary xylene from English gas-tar, orthoxylene may be estimated by difference, the two other xylenes and the paraffins having been estimated as above. But since toluene, cumene, and cymene are also acted upon by dilute nitric acid, samples containing these should be treated in the following way:—Employ part of method B to effect the separation of the paraffins and the paraxylene from the crude xylene; convert the meta- and orthosulphonic acids into their calcium salts, and afterwards into their sodium salts; concentrate the solution of the latter, when the ortho-salt will crystallize in large prisms, while the meta-salt remains in solution; concentrate the solution still more, and recrystallize the first and second crop of crystals. The ortho-salt will then be obtained in large, well-developed crystals, which are easily distinguished from the indistinct crystals of the meta-salt, if such are mixed with it. Scotch xylenes furnish the ortho-salt much less

easily than English ones, even when the latter contain much less ortho-xylene, probably owing to the complications caused by the presence of non-saturated hydrocarbons. Method B, and the additional method just described, are of little practical importance, since the buyer only wants to know the percentage of metaxylene; but method B is a good check upon method A.

Levinstein in this manner obtained the following result with different descriptions of commercial xylenes :—

Origin.	Sp. grav. at 19°.	Distils at °C.	Meta-xylene.	Para-xylene.	Ortho-xylene.	Paraffins.
Pure metaxylene obtained by method A	0·8668	142–143	100	0	0	0
English (from Manchester tar)	0·8629	134–140	87	6	4	3
English	.....	140–143	87	4	6	3
English	.....	141–145	83	5	7	5
English	0·8660	138–141	79	3	15	3
Scotch	0·8574	134–140	72	8	12	8
Unknown	.....	139–141	70	5	15	10
English and Scotch mixed	0·8605	134–141	81	10	3	6
English and Scotch mixed	.....	136–142	86	6	4	4
English and Scotch mixed	0·8613	136–141	86	6	2	6
English and Scotch mixed	.....	140–141	86	3	5	6
?	0·8600	136–142	85	6	3	6
Xylene from coal-gas	.....	138–144	47	8	13	26

Levinstein himself only claims approximate accuracy for his method. A. Reuter * objects to it that very dilute nitric acid does not fully remove the isomers of metaxylene, and that an acid of the concentration prescribed by Levinstein acts also upon metaxylene and oxidizes it into metatoluic acid. Moreover, paraxylene is acted upon by ordinary sulphuric acid, although less so than its isomers. The presence of paraffins greatly increases the resistance of all the isomers. Lastly, the paraffin can only be freed from the last traces of xylenes by employing a great excess of fuming sulphuric acid.

The analyses given by Levinstein are also at variance with the statement by Noelting, Witt, and Forel (Berl. Ber. 1885, p. 2068), that they always found at least 25 per cent. paraxylene in commercial xylol.

Radziszewski and Wispek † state that very small quantities of

* Ber. d. deutsch. chem. Ges. 1884, p. 2028.

† Ibid. 1885, p. 1280.

paraxylene can be detected in ortho- or metaxylene by treating the hydrocarbons with an insufficient quantity of bromine (*e. g.* 24 parts bromine to 10 parts of the hydrocarbons); in that case the paraxylene bromide separates first on cooling, in the shape of a pulverulent precipitate fusing at 143°·5.

A method for separating the two *trimethyl-benzenes* (pseudocumene and mesitylene) has been described by Jacobsen*. It is founded upon converting them into sulphamides, separating these by alcohol, and regenerating the hydrocarbons by fuming hydrochloric acid. Up to the present time there is no technical use for this method.

Testing of Crude Naphtha (first runnings &c.) for Final Products.

A paper on the valuation of crude naphtha &c. has been published by G. E. Davis †. He mentions that the method usually employed is to distil a quantity (generally 100 c. c.) in a tubulated glass retort, and to catch the quantity distilling over up to a temperature of 120° C., the bulb of the thermometer being immersed the whole time in the boiling liquid. The article is generally sold on the basis of an average yield of 30 per cent. at 120°, within a rising or falling allowance per degree, or every 1 per cent. within prearranged limits. This test has no recommendation except its simplicity; and if buyers do not receive a sample to judge for themselves, but only an account of the test, they may suffer great losses. Crude naphtha is valuable only for the benzene, toluene, and solvent naphtha it contains; but the distillation-test to 120° does not differentiate these products, nor does it take any account of the loss in washing with acid and alkali.—A much better test than the above is:—100 c. c. of the naphtha to be distilled in a 200 c. c. flask, with a thermometer arranged so that the bulb shall be just off the bottom of the flask. The distillate to be caught in a 100 c. c. graduated measure, and the yield at the following points taken: 100°, 110°, 120°, 140°, 170°, 200°. The quantity which shall have passed over at 140° is to be again distilled, and the yield at 100° and 120° noted. [This almost exactly agrees with the prescription given by the author as far back as 1867.] All which passes over

* Ber. d. deutsch. chem. Ges. 1876, p. 256; comp. Armstrong, ibid. 1878, p. 1697.

† Journ. Soc. Chem. Ind. 1885, p. 654.

up to 100° in the second distillation is called *benzol* (B); that which passes between 100° and 120° in the second distillation is called *toluol* (T). *Best naphtha* (N_1) is that which passes between 120° in the second and 170° in the first distillation; *second naphtha* (N_2) that caught between 170° and 200° in the first distillation; and *creosote* (C) the balance. The following are some tests made by this method:—

Spec. grav.	First distillation.						Second.		Products.				
	100°.	110°.	120°.	140°.	170°.	200°.	100°.	120°.	B.	T.	N_1.	N_2.	C.
0·886	2	22	42	67	88	94	23	53	23	30	35	6	6
0·893	11	30	50	72	88	95	27	56	27	29	32	7	5
0·903	2	14	23	56	78	92	23	42	23	19	36	14	8
0·915	0	2	11	39	73	94	7	26	7	19	47	21	6
0·917	2	16	34	57	75	87	22	43	22	21	32	12	13
0·940	2	10	21	42	59	69	23	36	23	13	6	17	10

This method is, however, not yet accurate enough. The redistillation of a large quantity of the different fractions gave the following results:—

B..... 85° 90° 95° 100° 110° 120°
2 48 71 80 90 95 per cent.

T..... 100° 110° 120° 130° 135°
47 75 86 94 96 per cent.

N_1 ..... 130° 140° 150° 160° 170° 180°
13 43 63 79 91 93 per cent.

N_2 ..... 160° 170° 180° 190° 200°
2 31 55 74 87 per cent.

The "creosote" crystallized into a solid mass [probably naphthalene]. The above shows that the "benzol" is only of 80 per cent., the "tuluol" is nearly a 50/90 benzol, the naphthas N_1 and N_2 are mixtures of solvent naphtha and light oil. Neither does the just-described method take into account the products eliminated by washing with acid and soda. In a special case 1600 gallons of crude naphtha, tested by that method, yielded:—

25 B, 23 T, 32 N_1, 10 N_2, 10 C.

After washing there remained 1200 gallons, which tested:—

26 B, 14 T, 24 N_1, 9 N_2, 27 C.

When this quantity was worked in a still of the best construction, it yielded :—

348 gallons 90-per-cent. benzol = 23 per cent.
362 gallons 50-per-cent. benzol = 24 per cent.
156 gallons solvent naphtha = 10 per cent.

Hence the test would have led one to suppose that much more solvent naphtha [and less 50-per-cent. benzol] would be obtained than was actually the case.

Davis therefore recommends the following method [which practically agrees with the general prescriptions given by the author in the first edition of this work, pp. 251 and 252] :—

200 c. c. of the crude naphtha are agitated with 20 c. c. concentrated sulphuric acid (rectified oil of vitriol) in a stoppered globular separating-funnel of 300 c. c. capacity. After agitating well for five minutes, allow to settle and run off the acid carefully, so that nothing is lost. (Sometimes two washings with 10 c. c. of acid each are preferable to one washing with 20 c. c.) Now wash twice with 30 c. c. of water, each time running off the wash-waters very carefully, then add 30 c. c. caustic-soda solution, of spec. grav. 1·060, and again wash with water. Pour the washed naphtha into a measuring-jar, and determine the percentage loss. All is now ready for the distillation. Measure off 100 c. c. of the washed naphtha, less the percentage loss, and place in a 200 c. c. flask fitted with a delicate thermometer and Glinsky's or Le Bel Henninger's fractionating-tubes (or any other, preferably Hempel's glass-bead tube, which has been shown in fig. 136, p. 492), connecting it with a Liebig's condenser of the ordinary pattern. Heat the flask with a rose-burner (fig. 134, p. 486), and so regulate the flame that a drop distils over about once in every two seconds. Carry the distillation on until the thermometer has risen to 120°, catching the distillate in a graduated jar. At this point change the receiver, and catch all that comes over up to 170°. The distillate to 120° consists substantially of benzene and toluene; the portion distilling between 120° and 170° is solvent naphtha, the remainder creosote. The "solvent" produced in this small apparatus will show the first drop at 125° and 90 per cent. at 100°, which is usually the quality worked for on the large scale. The composition of the distillate to 120° will vary somewhat with every sample of crude naphtha operated upon. In Davis's own case the quantities

yielded by each analysis were collected from many examples; and when mixed and tested in the usual way employed for 90-per-cent. and 50-per-cent. benzols, showed 64 per cent. at 100° and 93 per cent. at 120°. Davis states that it is easy, by means of this method, without any supervision, to run the specified quantities of 90's and 50's from the still direct, without any fear of mistakes. The following table shows the results of the older methods compared with those of the new method :—

Spec. grav.	Old method. per cent. at 120°.	Improved method (p. 498).					Davis's new method.				
		B.	T.	N_1.	N_2.	C.	Loss in washing.	per cent. at 120°.	Test at 100°.	per cent. solvent.	Creosote.
0·886	42	23	30	35	6	6	13·5	50	60 p. c.	23	27
0·902	31	19	22	35	15	9	18·5	46	59	19	36
0·908	29	17	23	39	13	8	10·5	45	64	23	32
0·924	32	30	13	27	15	15	16·5	47	58	13	40

In order to rapidly estimate the quantities of 90-per-cent. and 50-per-cent. benzol and toluol which can be run from the still, Davis has constructed the following tables :—

A. Mixtures of 90-per-cent. benzol with 50/90 benzol.

90-per-cent.	50/90.	First drop.	per cent. at 100°.	per cent. at 120°.
0	100	92°	50	90
5	95	92	51	92
10	90	91	51·5	92
15	85	91	53	92
20	80	90	55	92
25	75	90	60	93
30	70	90	65	93
35	65	90	67	94
40	60	88	69	94
45	55	88	70	94
50	50	87	71	94
55	45	87	73	94
60	40	86	76	95
65	35	86	78	95
70	30	86	79	96
75	25	85	84	96
80	20	85	84	97
85	15	84	86	97
90	10	84	88	dry
95	5	84	89	dry
100	0	84	90	dry

B. Mixtures of 50/90 benzol and commercial toluol.

50/90 Benzol.	Toluol.	First drop.	per cent. at 100°.	per cent. at 105°.	per cent. at 110°.	per cent. at 200°.
100	0	92°	50	68	80	91
95	5	93	45	64	76	91
90	10	94	33	60	73	90
85	15	94	30	58	73	90
80	20	95	28	57	72	90
75	25	95	26	55	71	90
70	30	96	22	48	67	90
65	35	96	19	47	65	90
60	40	96	15	46	65	90
55	45	97	12	44	65	90
50	50	98	8	42	64	90
45	55	98	4	34	57	90
40	60	99	0	26	56	90
35	65	100	0	25	55	90
30	70	100	0	23	53	90
25	75	100	0	21	53	90
20	80	100	0	16	48	90
15	85	101	0	14	46	90
10	90	102	0	13	45	90
5	95	103	0	10	44	90
0	100	103	0	0	39	90

C. Mixtures of 90-per-cent. benzol with commercial toluol.

90-per-cent. Benzol.	Toluol.	First drop.	per cent. at 100°.	per cent. at 105°.	per cent. at 110°.	per cent. at 120°.
0	100	103°	0	7	50	94
5	95	102	0	21	59	94
10	90	101	0	30	66	94
15	85	100	0	38	68	95
20	80	97	9	43	73	95
25	75	95	16	53	76	95
30	70	95	23	59	78	96
35	65	94	43	60	80	96
40	60	93	43	66	82	96
45	55	92	46	71	85	97
50	50	91	52	72	86	97
55	45	91	58	76	86	97
60	40	91	60	78	88	97
65	35	90	65	81	89	97
70	30	89	71	83	91	97
75	25	88	75	85	91	98
80	20	87	77	87	92	98
85	15	86	83	89	93	98
90	10	85	85	91	94	dry
95	5	84	88	93	95	dry
100	0	84	90	94	96	dry

ecuniary valuation of crude naphtha can be easily made, if per test has been applied. Davis quotes the following . A sample, tested by his new process, yielded :—

ss by washing..... 18½ per cent.
stillate to 120° ..... 45 per cent.
st of same $\frac{100°}{71}$ $\frac{120°}{94}$.
0 per cent. of 90-per-cent. and 50 per cent. of 50-per-cent.
., according to table A.]
)istillate to 170° ..... 10 per cent.
'est of same $\frac{126°}{0}$ $\frac{160°}{92}$.

The quantities actually obtained from the still were :—

90-per-cent. benzol 23 per cent. @ 1*s.* 7*d.* f. o. b. Goole,
50-per-cent. benzol 24 per cent. @ 1*s.* 4*d.* [casks free.
Solvent ..... 10·4 per cent. @ 9*d.*
Test of solvent $\frac{130°}{1}$ $\frac{160°}{94}$.
Loss by washing, 20 per cent.

Deducting 2*d.* per gallon for barrels, 2*d.* for carriage, and 1*d.* for sundries (leakages, super tares, &c.), this leaves at the works :—

			d.
90-per-cent. benzol	23 galls. at	1*s.* 2*d.*	= 322
50 „ „	24 „	11*d.*	= 264
Solvent	10 „	4*d.*	= 40
			626

$\frac{626}{100} = 6\frac{1}{4}d.$

per gallon of crude naphtha, out of which the rectifier will have to find, apart from the price of the crude naphtha, vitriol, soda or lime, wages, steam, repairs, depreciation, sundry charges, and his profit, if there be one.

Usually much less complicated methods than Davis's are employed for testing crude naphtha for its commercial value. The following empirical rules are taken from my own practice, and by means of them the results to be expected on the large scale can be very approximately inferred from laboratory distillations, which will take hardly a quarter of an hour. They were

elaborated before fractionating-bulbs had come into use, but they still hold good.

1st. 100 c. c. of the oil is distilled from a glass retort or fractionating-flask, and the distillate collected, (*a*) up to 140°, (*b*) from 140° to 170°. On each occasion, just as the required temperature is attained, the lamp is withdrawn, and the oil contained in the condenser is allowed to drain off before the receiver is changed; this makes a difference of several per cent. Suppose we have got 68 c. c. up to 140° and 86·5 c. c. up to 170°,—

2nd. The first distillate, in this case 68 c. c., is rectified, and that which passes over up to 100° is collected, allowing the oil to drain after removing the lamp. Suppose this to be 24 c. c. This figure, multiplied by 2, gives the quantity of 50-per-cent. benzol to be expected; in this case it is 48 parts from 100 parts of the crude oil.

3rd. The product (*a*) of the first distillation (up to 140°), in this case 68 c. c., less the 50-per-cent. benzol found according to rule 2, in this case 48 c. c., gives the volume of best naphtha, *i. e.* 68−48=20.

4th. The total product of the first distillation up to 170°, in this case 86·5 c. c., diminished by 15 per cent. for loss by purification (washing) and distillation, and by the quantities of 50-per-cent. benzol and best naphtha found according to rules 2 and 3, gives the quantity of burning-naphtha. In this case, 86·5−13=73·5; 73·5−68=5·5 parts for 100 crude naphtha. (A loss of 15 per cent. may be regarded as a maximum; with careful work it does not exceed 10 per cent.)

5th. The difference is the residue going to creosote oil. Thus in our case we find the following total:—

48	parts	50-per-cent. benzol,
20	,,	best naphtha,
5·5	,,	burning-naphtha,
15	,,	loss,
11·5	,,	creosote oil.
100·0		

If less volatile oils have to be tested, 200 or 300 c. c. are distilled up to 180°, and the residue is submitted to exactly the same operations and calculation-rules as have just been described.

At the present time most tar-distillers test their crude naphtha by means of fractionating-bulbs (Le Bel's, Hempel's, &c.), and thus obtain results very nearly indicating the probable yield on the large scale.

Storage and Carriage of Benzol, &c.

For storing benzol and naphtha, only wrought-iron vessels are suitable; they may be of any shape and size. Since tar-oils pass through the joints much more easily than water, both as liquids and as vapour, and since their vapours form with air easily inflammable or even explosive mixtures, the store-tanks must be constructed with special care and must be protected against any contact with fire. They are put together in as large plates as possible, to lessen the number of joints; and these are very carefully riveted and caulked. Only first-class workmanship will ensure that no evaporation takes place. The tanks are painted outside with good tar-varnish (p. 277), but preferably not until the joints have somewhat rusted and thus have become tighter. They are provided with a hole for filling them, a man-hole, and two taps—one a little above the bottom for the ordinary filling of the sending-out vessels, the other in the bottom itself for occasionally drawing off any water and mud. The tanks are mostly placed on pillars high enough to fill the casks directly. But at some places tanks placed in the open air, and partially underground, are preferred, on account of the diminished danger of fire. In any case, for the same reason, the benzol storehouse ought to be at some distance from any fireplace; and it is best to employ an open shed for it. Lighting it is mostly unnecessary; in case of need this can be done only from the outside by means of reflectors.

The carriage of benzol is effected in good oak casks, *e. g.* spirit-puncheons, preferably made tighter by washing with a dilute solution of glue, like petroleum-barrels; but still better are tightly riveted iron casks.

For the momentary stoppage of leaks soap can be employed, which is not acted upon by naphtha; but it does not stand any considerable pressure. Glue, too, is not acted upon.

Applications of Benzol and Naphtha.

Levinstein * estimates the productive capacity of the United Kingdom (in 1886) at nearly 3 million gallons, of which quantity Germany takes 1½ millions (in addition to ½ million home-production), England ½ million, France and other countries the remainder.

Most of this is employed in the manufacture of colouring-matters, in the shape of 90-, 50-, 40-per-cent. benzol, &c., and of nearly pure benzene, toluene, and xylene.

It is reliably estimated † that the German colour-works in 1880 consumed monthly 1020 tons of benzol, nine-tenths of which came from England. Of this about two thirds was benzene, one third toluene. The employment of xylene in 1880 amounted to from 4 to 6 cwt. per diem.

Nitrobenzene made from the purest benzene is sold by the name of "huile de mirbane," as a substitute for oil of bitter almonds in cheap perfumery.

Benzol also very frequently serves as *a solvent*, both in the manufacture of colours and otherwise. Of the greatest importance is its preeminent dissolving-power for fatty matters, upon which is based its extensive employment as a detergent; but petroleum "benzin" or "benzoline" largely competes with coal-tar benzol in this respect.

A good domestic detergent consists of a mixture of 25 parts benzene, 5 ether, and 5 absolute alcohol. A detergent for removing fat-, tar-, resin-, wax- and acid-spots from all sorts of fabrics is prepared by adding 10 parts of benzol to 100 parts of 95-per-cent. alcohol, and 35 parts of liquor ammoniæ of spec. grav. 0·875. "Benzol-magnesia" (that is, burnt magnesia soaked with benzol) is excellent for removing grease-spots from fabrics, ivory, &c.

Benzol also dissolves many resins, caoutchouc, gutta-percha, alkaloids, &c. Against spirits of turpentine it enjoys the advantage of not being oxidized by the oxygen of the air, and of being easily recoverable by distillation.

In the manufacture of india-rubber goods, as well as in most other cases where benzol and its homologues serve as solvents, it would be too expensive, and sometimes even objectionable on

* Journ. Soc. Chem. Ind. 1886, p. 351.

† Chemische Industrie, 1880, p. 416.

account of too great volatility, to employ products consisting mainly of benzene and toluene, such as form the staple article required for colour-making. Hence the cheaper products distilling at a somewhat higher temperature, and essentially consisting of the three xylenes, along with some trimethylbenzenes &c., are specially collected and sold as *solvent naphtha*.

We have seen on pp. 460 & 479 what are the special requirements of English india-rubber manufacturers, whose process has been described by Kniess *. Since it now pays to extract the xylenes for colour manufacture, the solvent naphtha is of different quality to what it used to be, and such naphtha is hardly as valuable for india-rubber manufacture as the old article (Journ. Soc. Chem. Ind. 1884, pp. 81 & 82). Heren † gave a table of the solubilities of different descriptions of india-rubber in "benzol," which shows variations of from 6 to 25 parts of india-rubber to 100 of "benzol." But whether he means pure benzene, or commercial benzol, or solvent naphtha, does not appear. 90-per-cent. benzol serves for preparing the finest japans and varnishes, *e. g.* for photographic purposes.

Of other applications of benzol we will mention that for extracting iodine ‡ (which has hardly ever been practised), in making beet-root sugar §, and as a remedy against eruptions of the skin, itch, and parasites of domestic animals (in the shape of a mixture with soft soap).

The oils distilling just after benzol are very well adapted for *carburetting gas, i. e.* for increasing its illuminating-power by the vapours of hydrocarbons; this is favoured by their low price and not too high degree of volatility. Almost from the beginning of the industry of coal-gas, inventors have been busy in the direction of enriching it, by mixing it with the vapours of more light-giving substances; and the question whether this is feasible and economical is not absolutely decided even at the present time.

Whether carburetting the gas is a profitable process or not, cannot be decided generally, but only in each special case, by taking into account the illuminating-power and price of the gas, and the price of the carburetting naphtha. Coal-tar naphtha is much better adapted for this than petroleum spirit, on account of

* Dingler's Pol. Journal, cxxxviii. p. 442.
† Dingler's Journal, ccxxi. p. 391.
‡ Wagner's Jahresb. 1866, p. 182. § Ibid. 1874, p. 674.

its larger percentage of carbon. That poor gas can be very much improved by carburetting is beyond any doubt; but it is another question whether it is not more economical to make richer gas to begin with. The question is certainly not decided by the fact that some eminent gas-engineers have pronounced against carburation as a plaything or the like; for they are interested parties, and even the miscarriage of very many attempts does not refute the opinion that in other conditions the result would be favourable *. In the case of "water-gas," which by itself is not luminous at all, and hence *must* be rendered so in one way or another, the question of carburetting has been worked out in America on a colossal scale, and hundreds of gas-works are there attesting its feasibility every day. But it is certainly rather a different question, whether carburation is the proper thing for ordinary coal-gas or not.

This subject was treated *in extenso*, and decided in favour of the principle of carburation in 1865 by Dr. Letheby †. We shall not attempt to go into the detailed description of the innumerable carburetting-apparatus, but content ourselves with enumerating some of the patents, part of which refer to the production of illuminating-gas from air and inflammable vapours. Some of the older patents are those by:—Mansfield (B. P. 11960, 1847); Rolands (B. P. 1210, 1855); Longbottom (B. P. 660, 1854); Lacarrière (Bull. Soc. d'Encourag., Mai 1857, p. 21); anonymous (Wagner's Jahresb. 1861, p. 683); Brooman (B. P. 2770, 1862); Gloessiner and Farenne (B. P. 67, 1862); Evans (B. P. 2618, 1861); Mongruel (B. P. 731, 1862); Wells and Myers (B. P. 2998, 1865); Reissig (Journ. für Gasbeleuchtung, 1865, p. 396); Phillipps (Wagner's Jahresb. 1870, p. 733); Jungling (Bull. Soc. Chim. 1873, xx. p. 331); Parody (ibid. p. 335); Young and Kitt (B. P. April 3, 1872); Bizot, Akar, and Co. (Fr. P. 94576, 1872); Fogarty (Journ. f. Gasbel. 1874, p. 248); Hoyer and Studelmann (G. P. 4723); Livesey and Kidd (G. P. 2075); Stephan (G. P. 3856); Anders (G. P. 11107); Richter and Friebel (G. P. 12150).

In England, according to the Index of Patents, in the years between 1859 and 1866 not less than 151 patents were taken out

* Comp. G. E. Davis, Journ. Soc. Chem. Ind. 1886, p. 2.

† Chem. News, xi. p. 276.

for carburetting gas. Since 1881 there have been issued the following patents :—

1. *For carburetting ordinary coal-gas.*—Lascols (G. P. 17495); Badt (G. P. 15902); MacDonald (G. P. 16642); Weston (G. P. 16458); Delau (G. P. 16669); Richter (G. P. 16873); Wittamer (G. P. 18248); Vale (G. P. 19012); Hohmann (G. P. 22740); Vigreux (G. P. 20853); Decker (G. P. 26333); Thomas (B. P. 3359, 1883); Sutton (B. P. 4747, 1883); Delamar and Malandin (B. P. 15248, 1885); Little (B. P. 1578, 1884; 17108, 1885); Lindemann (G. P. 32261); P. v. Richter (G. P. 28784); Wallis and Ratcliffe (B. P. 1650, 1886); Parkes (B. P. 2950, 1886); H. E. A. Wallis (B. P. 10778, 1886).

2. *For carburetting compressed gas.*—Riedinger (G. P. 19521); Dery (B. P. 8816, 1885).

3. *For carburetting air.*—Faignot-Chavé (G. P. 16013); Bum (G. P. 16441); Wittamer (G. P. 18248); Pollack (26170; 30184); Schoth (G. P. 26869); Muir (25960); Girandon (B. P. 4856, 1883); Henning (B. P. 12481, 1884); Debouttevillle and Malandin (B. P. 6652, 1884); Schnell and Read (B. P. 690, 1885); Dubos (G. P. 29632); Carmien (G. P. 33202); Bennett (B. P. 2258, 1886); H. Howell (B. P. 11713, 1886); Foord and Paddon (B. P. 11664, 1886); Girandon (Dingl. Journ. vol. cclxii. p. 321); J. Roots (B. P. 13967, 1886); G. Lestang (Revue indust. 1886, p. 273); L. Fuchs (G. P. 35924); M. Herzog (Amer. P. 307042).

Dr. Letheby's specification, which had been adopted by the London lighting authorities (p. 459), must yield a product essentially consisting of xylene. He did not assume this to act better than benzene or toluene; but he selected that product because it was not then employed at colour-works and consequently was lower in price. By Knublauch's investigations * it has been ascertained that, in fact, benzene, for equal weights, imparts the greatest illuminating-power to gas, and that the higher homologues only act in proportion to their molecules, only the carbon of the benzene nucleus being set free in a luminous form, whilst that of the methyl groups is burned directly to carbon dioxide. But it seems out of the question to employ benzene itself for carburetting either coal-

* Berl. Ber. 1881, p. 240.

gas or air (although the first who manufactured benzene on an industrial scale, Mansfield, had the latter object in view), as the high value of benzene will always be an impediment to such an employment, even at the present depressed prices.

It is well known that gas, when being passed in a continuous stream through a liquid containing several volatile substances of different boiling-points, will in the first instance carry away more of the more volatile portions, and that the composition of the remaining liquid must consequently undergo constant changes. This is a drawback to all carburetting liquids practically available, as they are all such compound substances. Thus carburetting naphtha made by Letheby's specification, in experiments made by G. E. Davis*, yielded at first 3·25 gallons of the lighter oils to 10,000 cubic feet of gas, but after a time scarcely anything was vaporized, and the boiling-points of the remaining naphtha were much higher. Exactly the same thing happened with 50/90 benzol, and with 90-per-cent. benzol (which under similar circumstances yielded about 15 gallons to 10,000 cubic feet of gas). The same happens with gasoline and other mixtures of fatty hydrocarbons. The irregular evaporation of the fluid is a serious drawback in the case of all mixed liquids, but it would not apply to a uniform substance like naphthalene. Davis found that the residual fluids contained in absolute quantities more of the higher-boiling hydrocarbons than originally; evidently the gas took up the benzene by preference, and deposited its own hydrocarbons of lower vapour-tension in the carburetting fluid, thus making it more and more unsuited for enriching the gas.

The carburation takes place either at the burner itself, or at the gas-works. In the former case it is troublesome to constantly replenish the reservoirs with the carburetting-liquid. There is rather less trouble in that respect, but more in others, in the case of naphthalene, as described, p. 419. The apparently easier plan of carburetting at the gas-works involves the necessity of so treating the mixture that the gas may not deposit the carburetting-substances on its way through the network of pipes. The American water gas-works therefore "fix" the carbon of the hydrocarbon vapours mixed with the water-gas by passing the mixture through red-hot retorts, or in some similar manner. In

* Journ. Soc. Chem. Ind. 1886, p. 4.

this process no doubt pyrogenetic changes are effected similar to those described p. 90 *et seq.*

The highest-boiling oils obtained by the steam rectification, if they cannot be worked in with solvent naphtha, are sold as *burning-naphtha*. Coal-tar naphtha, whether pure or mixed with petroleum spirit, is not adapted for burning in ordinary lamps or at all in closed rooms, but merely for special lamps, without wick or chimney, which do their duty even in strong wind and rain, and hence serve for lighting factories, courtyards, booths at fairs, &c. in lieu of gas. Good naphtha, no doubt, gives a very fine white light. Figs. 137 and 138 show a suitable lamp for this purpose (Holliday's patent). Fig. 137 is the lamp itself, on a scale of

Fig. 137.

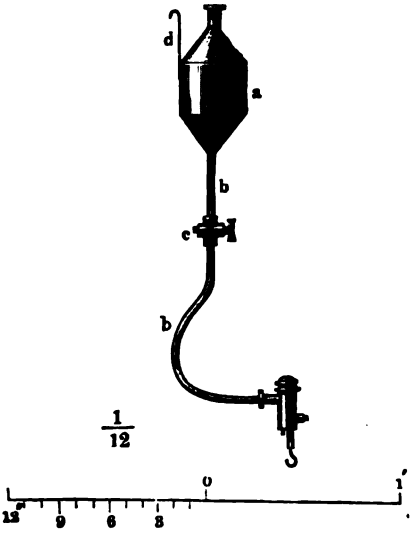
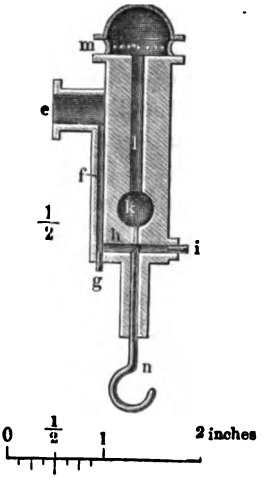


Fig. 138.



1 : 12; fig. 138, the burner, on a scale of 1 : 2. *a* is the vessel for naphtha, from which a thin tube *b* leads downwards; the cock *c* regulates the outflow; the tube *b* is almost entirely filled up by a round wick, which extends nearly to the burner, and of which the sole purpose is to make the outflow of the naphtha gradual. The hook *d* serves for hanging up the lamp. In the burner we notice the lateral tube *e*, communicating with *b*, and introducing the naphtha. This flows downwards in the narrow

channel *f*, which is closed by the thin screw *g*, the channel *h* being closed by *i*. The naphtha must rise from *h* in the fine central channel, leading to a hole *k* across the burner. Here it would run off, if the burner had not been previously heated sufficiently to evaporate it at once. The vapour, mixed with the air entering at *k*, rises in the central channel *l*, issues through the holes in the burner-head, and, on being lighted, produces a star-shaped flame. The draught generated by this suffices for preventing the naphtha-vapour from issuing into the open air instead of into the channel *l*. The screw *n* permits regulating the orifice of the fine channel between *h* and *k*. Here also a small cup may be fixed for some naphtha to be lighted in order to effect the first heating of the burner, the tap *c* being then closed. Otherwise the burner-head is put into some fire till it is warm enough. When this is the case, the tap *c* is opened, the vapour issuing out of the holes *m* is lighted, and the size of the flame regulated by *c*. Once lighted, the burner always remains warm enough.

When burning-naphtha can be sold in quantity, it is advisable to mix it with *petroleum spirit*, which in this case is an improvement, and especially tends to keep it colourless. The petroleum spirit can be pumped into the still after the solvent naphtha has come over, and can be distilled along with the burning-naphtha. Care should be taken that about equal parts of coal-naphtha and petroleum spirit distil together; the smell of the latter will then not be perceptible. Or else the petroleum spirit is mixed with the naphtha after distillation. The best descriptions of petroleum spirit for this purpose are those which give off very little below 100°, but nearly the whole up to 170°.

We conclude with a *synoptical table of the distillation of coal-tar*, which is to represent one of the modes in which this manufacture may be carried on; but it is hardly necessary to say that I do not mean to lay it down as the best in all cases, the preceding treatise offering many equally acceptable deviations in particular instances.

SYNOPSIS OF THE DISTILLATION OF COAL-TAR.

[The numbers in brackets denote the pages of this treatise where the operations referred to are described in detail.]

DEHYDRATION, *a.* by standing [195] .....
b. during the heating-up [197] ..... } AMMONIACAL LIQUOR.

DISTILLATION.

I. *Fraction, up to* 170 { Ammoniacal liquor ..... / *First runnings* [227, 429], rectified [424], yield :—

1. Product up to 110°, chemically washed [432], distilled by steam [448] yields *a* .....
b. Weaker benzol, goes to I. 2. } 90-PER-CENT. BENZOL.
2. Product up to 140°, treated like 1, yield *a* ...
b. ..... 50-PER-CENT. BENZOL.
c. Intermediate fraction, is redistilled.
d. ..... } SOLVENT NAPHTHA.
3. Product up to 170°, treated like 1 and 2, yields *a*
b. ..... BURNING-NAPHTHA.
c. Residue, goes to II.

II. *Fraction, from* 170° *to* 230°. *Middle oil* [234, 366]. Washed with caustic soda [371], yields :—

1. Oil, distilled in the light-oil still, yields
a. Distillate up to 170°, goes to I. 3.
b. „ „ 230°, yields [407]..... ..... NAPHTHALENE.
c. Residue, goes to III.
2. Alkaline liquor, decomposed by carbonic acid [377], yields :—
a. Aqueous solution of sodium carbonate, causticized by lime and used over again.
b. Crude carbolic acid, is purified [380] and yields *a* ..... CARBOLIC ACID.
β. Waste oils, go back to II.

III. *Fraction, from* 230° *to* 270° = *Heavy oil* [collected till solid matters begin to crystallize, pp. 235, 328].
Can be treated for naphthalene [407], usually only employed as ..... } CREOSOTE OIL.
Or else separated [235] into *a* .....
b. [335] ..... LUBRICATING-OIL.

IV. *Fraction, Anthracene oil* [296].
Filtered, or cold-pressed [298], yields :—

1. Oils, are redistilled and yield [309]
a. Solid distillate, treated along with IV. 2 ;
b. Liquid distillate, goes to III. *b*, or is redistilled ;
c. Residue (pitch, coke, &c.).

2. Residue, is hot-pressed [300] and yields
   a. Oils, treated like IV. 1;
   b. Crude anthracene, washed with naphtha &c. [303] yields
      α. ..... ANTHRACENE.
      β. Solution, is distilled and yields
         aa. Naphtha, used over again for washing;
         bb. Phenanthrene &c. is burnt to [165] ..... LAMPBLACK.

V. *Pitch* [270]. Employed for patent fuel [273] or varnishes &c. [277]..... PITCH.
Or else distilled [284], yielding:—
1. Crude anthracene, treated like IV. 2;
2. Lubricating oil, goes to III. *a*, resp. III. *b*;
3. Residue [291] ..... COKE.

CHAPTER XII.

SOURCES FROM WHICH AMMONIA IS OBTAINED.

Ammonia is formed in many cases where nitrogen and hydrogen meet in the nascent state, even when only one of these substances is in that state. Thus, for instance, ammonia is formed by passing a mixture of hydrogen and "nitrous vapours" (*i. e.* a mixture of the oxides of nitrogen) through a gently heated tube, filled with porous substances, especially platinum sponge. Cold platinum sponge is heated to redness in such a mixture, and causes the combination of N and H to NH_3 with great violence. Especially nascent hydrogen causes the formation of ammonia from nitrates and nitrites, also from the free acids, but best in an alkaline solution, when the hydrogen is set free by aluminium or a mixture of zinc and iron. In concentrated solutions iron alone causes the decomposition of nitrates in the presence of alkali*. Sodium sulphide in the presence of sodium hydrate also furnishes ammonia by heating with nitrate; the conditions of this reaction, a very important one in the manufacture of caustic soda, have been accurately investigated by Lunge and Smith†.

Atmospheric nitrogen, according to Schönbein, directly unites with the elements of water and forms ammonium nitrite,

$$2N + 2H_2O = NH_4NO_2;$$

this reaction occurs, to a slight extent, every time when water evaporates with excess of air. The combination of free nitrogen and hydrogen is accelerated by the electric spark or the silent electric discharge, but it is always very far from being complete,

* Lunge, Journ. Soc. Chem. Ind. 1884, p. 287.

† Journ. Soc. Chem. Ind. 1883, pp. 460 and 525.

as the counter-reaction of decomposing the NH_3 into its elements very soon sets in.

Ammonia is further formed by the decomposition of cyanogen compounds under the influence of moisture. A solution of potassium cyanide is quickly decomposed in this way,

$$KCNO + 2H_2O = KHCO_3 + NH_3.$$

The cyanides also yield their nitrogen in the shape of ammonia in ontact with superheated steam; several processes for technically obtaining ammonia are founded on this reaction.

In the economy of nature the formation of ammonia during the decay of nitrogenous organic substances is the most important source of that compound—all the more as the naturally occurring nitrates are undoubtedly for the most part formed by the oxidation of such ammonia. The formation of ammonia is most easily understood in the decomposition of urea, which, being the amide of carbonic acid, needs only to combine with water in order to pass over into ammonium carbonate,

$$CO(NH_2)_2 + 2H_2O = CO_3(NH_4)_2.$$

But the other organic substances in putrefaction also yield part, or sometimes the whole, of their nitrogen in the shape of ammonia.

For technical purposes it is most important that nitrogenous organic substances, when heated in the absence of air, that is in destructive distillation, also yield their nitrogen, at least partly, in the shape of ammonia. Although animal matters contain much more nitrogen than vegetable ones, it is a derivative of the latter, namely coal, which supplies most of the ammonia used in the arts and manufactures, when subjected to destructive distillation for the purpose of obtaining illuminating-gas and coke. But probably a very large portion of the nitrogen of coal belongs to the animal remains buried in it, and to atmospheric ammonia absorbed, as we shall see later on.

We shall now separately treat of the various technical sources of ammonia.

A. Natural Occurrence of Ammonia.

Ammonia, especially as carbonate, is found almost everywhere in soil, water, and air, as a product of the decomposition of organic bodies, but in very slight traces. Although the growth of plants seems altogether to depend upon the ammonia thus presented to

them and upon the nitrates formed by the oxidation of that ammonia (along with that formed by the electric discharge), yet this ammonia is diluted to such an enormous extent that it will ever be out of the question to recover it in substance.

In some cases rather more ammonia is collected in one spot, owing to the absorptive faculty of some kinds of clay, of peat, &c. But even in such cases it would seem hopeless to recover it in a direct way, although this sometimes becomes possible indirectly, when the materials in question are subjected to processes for recovering other useful substances, *e. g.* peat to dry distillation, for the purpose of extracting oils and paraffin. Indeed, the principal source of ammonia, coal, seems to owe its nitrogen in a great measure to the absorptive faculty of some forms of decaying organic matter for the ammonia of air, and of that produced within its own mass.

A more direct opportunity of recovering ammonia is presented when, under favourable circumstances, the ammonium salts formed in the decomposition of organic matter are not, as is usual, at once diluted and dispersed, but are allowed to collect and concentrate. Thus ammonium carbonate in substance is found in the *guano deposits* on the west coast of South America, sometimes in such large quantities that it can be exported to Europe. Such ammonium salt first appeared in Germany in 1848. The analysis of a sample proved that it consisted essentially of ammonium bicarbonate, mixed with some insoluble matter.

Native ammonium sulphate is contained in the Tuscan "*suffioni*," and forms a by-product in the manufacture of boric acid. It is also found in large quantities in the soil surrounding the lagoons, and may have been produced by decomposition of nitrogenous organic matter in the rocks composing the Tuscan hills. In an experiment made at Travale, four suffioni in 24 hours yielded 5 tons of salts, containing 3 cwt. boric acid, $1\frac{1}{4}$ tons of ammonium sulphate, $1\frac{3}{4}$ tons of sulphate of magnesia, $\frac{3}{4}$ ton of sulphate of iron and manganese. Somewhat considerable quantities of ammonium sulphate are brought into the market from this source.

Native ammonium chloride, along with sulphate, is sometimes collected in the neighbourhood of *volcanoes*, as Vesuvius and Etna. This occurrence is never of any consequence; but it is asserted that the name "ammoniac" is derived from "sal armeniacum" or "armoniacum," that is, sal-ammoniac collected at the Armenian

volcanoes. Since, however, the Arabian chemist Geber, as early as the eighth century after Christ, prepared sal-ammoniac from urine and common salt, in the way it is done even now in the East, it would seem very doubtful whether sal-armoniacum should be looked upon as a volcanic product.

In any case a very small proportion of the ammonium salts occurring in commerce is derived from native sources.

B. Ammonia formed from the Nitrogen of Atmospheric Air.

It is a well-known fact that ammonia can be formed directly from its elements, more especially by the electric discharge*; also in the process of combustion of a mixture of hydrogen, oxygen, and nitrogen (Saussure). But in both cases the inverse reaction, that is the decomposition of ammonia by heat and electricity, is far more powerful (comp. later on); so that it seems a hopeless task to manufacture ammonia directly from atmospheric nitrogen, unless some special agency can be found which favours the formation and suppresses the decomposition of ammonia. Very confident assertions have been made from time to time in that respect by various inventors, but nothing has ever come from it. The small quantities of ammonia, *bonâ fide* obtained in the experiments, may sometimes have been pre-existent in the materials employed; and so much is certain, that none of it has ever been brought into commerce.

H. Fleck† describes the following experiment. When hydrate of lime is brought to a red heat, its chemically combined water is split off, and in this state is more prone to be decomposed. If, therefore, a mixture of nitrogen and carbon monoxide is present at the same time, the following reaction takes place:—

$$2N + 3CO + 3H_2O = 2NH_3 + 3CO_2.$$

This reaction was utilized by passing atmospheric air over charcoal contained in an iron tube heated to a red heat; the issuing gas was passed through boiling water, and then through a porcelain tube filled with hydrate of lime. Whenever the latter tube was heated to a temperature "between dark red and bright red," considerable quantities of ammonia were formed (in one case 16 grains

* Comp. Donkin, Proc. Roy. Soc. vol. xxi. p. 281.

† Die Fabrikation chemischer Produkte aus thierischen Abfällen. Braunschweig, 1862, p. 48.

NH_4Cl from 15 cubic feet of air); but a little above or below that temperature the evolution of ammonia was very slight, or ceased altogether. Fleck himself published his experiments only as a stimulus for further trials. Weinmann *, on repeating Fleck's experiments, could not obtain any ammonia; but this may have been owing to his not having hit the precise temperature required.

Maxwell Lyte † passes a mixture of steam and nitrogen over certain alloys or other compounds of the metals of the alkalis or the alkaline earths, or zinc, namely alloys of antimony, bismuth, arsenic, or tin with sodium, potassium, or zinc. The hydrogen liberated is supposed to unite with the nitrogen and to form ammonia.

Ed. Solvay ‡ impregnates coke with magnesium chloride and heats the mixture by the help of a blast. The products of combustion contain sal-ammoniac, which is to be recovered by condensation. The priority of this invention is claimed by R. Wagner §. Probably any ammonia formed in Solvay's experiments was derived from the nitrogen contained in coke (comp. later on).

G. Swindells (B. P. June 21, 1876) passes a mixture of air and steam over red-hot coals, and the resulting mixture of gases through a solution of caustic soda. The escaping mixture of hydrogen and nitrogen is to be united into ammonia by heating in chambers filled with burnt clay. [In all likelihood the ammonia found by Swindells was likewise formed from the nitrogen of the coal.]

J. P. Rickman (B. P. 3341, 1878) employs slanting retorts, made of iron or fire-clay, of an elliptical section, filled with coke or spongy iron, and heated to about 550° C. At the lower end a mixture of steam and air is blown in; the steam is decomposed, and the free hydrogen combines with the nitrogen to form ammonia, which issues at the upper end of the retort, mixed with the excess of steam.

A modification of this proposal was patented by J. P. Rickman along with J. B. Thompson in 1880 (G. P. 10889). They expose coal to a slow combustion with access of air and steam in regulated quantities.

* Ber. deutsch. chem. Ges. 1875, p. 977.
† Bull. Soc. Chim. 1876, xxv. p. 427.
‡ Ibid. p. 527.
§ Jahresb. f. chem. Technol. 1876, p. 444.

G. Th. Glover (B. P. 1890, of 1880) passes combustion-gases, containing much nitrogen, mixed with steam and hydrochloric acid, over red-hot coals or bituminous shale. The ammonium chloride formed is to be condensed by cooling, or to be passed into sulphuric acid.

To the proposals of Rickman, Thompson, and Glover we must apply exactly the same observation as to that of Swindells.

H. Endeman (Amer. Ch. Soc. J. vol. viii. p. 47) has observed the occurrence of ammonium thiosulphate as a condensation product from a gas-generator in which a mixture of air and steam was forced through anthracite coal, and he believes that the sulphur was derived from the anthracite coal, the nitrogen from the atmospheric air, and the hydrogen from steam. There is, however, no proof whatever given that the coal did not contain sufficient N to account for the NH_3 formed.

G. S. Johnson* asserts that ammonia is formed, if nitrogen, prepared by gently heating a mixed solution of potassium nitrite and ammonium chloride, is mixed with hydrogen, and the mixture is passed over red-hot platinum sponge; or else, if such nitrogen is passed over cold platinum sponge charged with hydrogen. No ammonia was formed when the nitrogen was first heated in a red-hot tube, or when it was obtained by passing atmospheric air over red-hot copper. From this Johnson concludes that nitrogen, like phosphorus, occurs in two modifications, only that formed in the cold being "active." These assertions were tested by Miss K. I. Williams and Ramsay†, but with a negative result. The total of "active nitrogen" found in 7·7031 litres of nitrogen prepared in the cold, as tested by the formation of NH_3, was only 0·000055 gram—that is, so slight a quantity that it must be attributed to accidental impurities not entirely removed by washing the gases. Johnson's statements have been also contradicted by Baker‡.

Several inventors aim at utilizing the intervention of the *boride of nitrogen* for forming ammonia. Thus N. Basset (B. P. 4338, 1879) heats coal impregnated with boric acid, and covered with a layer of magnesia, lime, oxide of manganese, &c., in a retort, and passes nitrogen over the mixture. When a sufficient quantity of

* Chem. News, vol. xliii. pp. 42 and 288.
† Journ. Chem. Soc. 1886, Proceed. p. 223.
‡ Chem. News, vol. xlviii. p. 187.

nitrogen boride has been formed, steam is introduced, and the ammonia now formed is carried away.

G. N. Tucker (G. P. 13392) mixes carbon, impregnated with borates, with alkaline carbonates, or the oxides of manganese, antimony, iron, titaniferous iron, or with the borates of these metals. These are exposed to a red heat in retorts; gas rich in nitrogen is passed in, so that the nitrogen combines with boron; then steam is passed in, which is decomposed by the carbon or the metal, and supplies the hydrogen necessary to form ammonia. Or else air or nitrogen and steam are mixed before introducing into the retort, in the proportion of 3 vols. H_2O to 1 vol. N. The borates and the metallic oxides contained in the residue are to be used over again. The gas is purified by milk of lime from carbonic acid, hydrogen, sulphide, and tarry substances.

A number of inventors invoke the aid of electricity. Thus Th. G. Young (B. P. 1700, 1880) passes electric sparks through a mixture of 3 vols. H and 1 vol. N.

W. Müller and E. Geisenberger (G. P. 11489) employ combustion gases, which are freed from carbon dioxide by means of lime, as a source of nitrogen. Hydrogen is to be obtained by the action of steam on red-hot coke. The mixed gases are to be united by the electric spark. Another proposal of the same inventors (G. P. 12364) is: passing the gases, obtained by heating alkaline nitrates, along with steam, over red-hot coal. The alkaline residue is to be reconverted into the original salts by the joint action of oxygen, nitrogen, and the electric current.

The Société l'Azote (G. P. 17070) aims at combining the nitrogen of air with the hydrogen of water by the action of porous substances and of electricity. Melted zinc is run into two furnaces kept at a red heat; into one of them is passed air, and water into the other. In both cases zinc oxide is formed; and there is liberated nitrogen on one side, hydrogen on the other. The gases are passed through dust-chambers to deposit zinc oxide, and thence through retorts containing titaniferous iron-sponge. Here the nitrogen is first absorbed, and is then converted into ammonia by hydrogen. The formation of ammonia is promoted by employing in the retorts a mixture of iron with other metals, whereby an electric current is said to be produced (!). They also employ platinized coal, into which is forced first nitrogen, then hydrogen, at a pressure of ten atmospheres.

Twinch (B. P. 3712, 1881) passes a mixture of steam, atmospheric air, oxide of nitrogen, and caustic-soda solution into a cylinder filled with granulated zinc. The oxide of nitrogen takes up the oxygen of the air, whose nitrogen then forms ammonia.

C. Ammonia formed from Atmospheric Nitrogen by the Intervention of Cyanides.

It has long been known, by experiments first made by Desfosses and Fownes, and confirmed by Bunsen and Playfair and other chemists, that nitrogen directly combines with carbon and the alkaline metals, but only at a very high temperature. Bunsen and Playfair have shown that in blast-furnaces, where these conditions are present, very considerable quantities of cyanides are formed. Their observations have been turned to practical account for the production of crude cyanide of potassium and of prussiate of potash; but this proved to be a failure in a manufacturing sense, as the very high temperature required (a full white heat) caused an excessive consumption of fuel, and wear and tear of the vessels employed, and as the reaction was very imperfect, owing to the fusing and volatilizing of the potash.

In 1860 * Margueritte and Sourdeval found that caustic baryta is much more active towards nitrogen than potash, because it is neither fusible nor volatile: the former quality prevents the external fusion of the mass, whereby the action of the gases on the interior is impeded; the latter prevents loss by volatilization—both very awkward drawbacks in the case of potash. Still, the manufacture of cyanides or ferrocyanides by the baryta process would seem to be too difficult; but Margueritte and Sourdeval at once aimed at forming the cyanide only as an intermediate product, and utilizing it for the formation of ammonia by the action of steam, thus:—

$$Ba(NC)_2 + 4H_2O = 2NH_3 + Ba(OH)_2 + 2CO.$$

They made a mixture of native barium carbonate with coal-tar, pitch, and saw-dust, with or without iron filings, which was strongly ignited in a fireclay retort till the barium carbonate had been converted into a porous mass of barium oxide. Through this they passed at the proper temperature a slow current of air, whose oxygen had been previously converted into carbon monoxide by

* Compt. rend. vol. 50. p. 1100; B. P. 1027, 1860.

red-hot coal: thus barium cyanide was formed. This was cooled down to 300°, and steam was passed through. All the nitrogen of the cyanide is evolved as ammonia, and the barium hydrate remaining behind can be used over again.

This process did not pay, owing to technical difficulties, and seems to have been neglected. Moerman-Laubuhr, in 1875, took out a French patent * for the following process:—

Bricks are made of pulverized charcoal or coke, and alkaline carbonates, and are exposed in a small blast-furnace to the action of air, previously deprived of oxygen by red-hot coal; the cyanide collects in the melted state at the bottom, and is tapped off from time to time; whereupon it is converted into ammonia by various methods, unnecessary to describe here, as the process evidently turned out a complete failure.

Margueritte and Sourdeval's process was taken up again by L. Mond (B. P. 433, 1882), who carries it out in the following form. The barium carbonate is powdered and incorporated with small coke from pitch or oil residues, charcoal, pitch, tar, paraffin residues, and so forth. In lieu of barium carbonate it is possible to employ a solution of its oxide or salts, or of alkaline oxides or salts; for instance, the solution obtained by lixiviating the used briquettes. The most advantageous proportions are :—32 parts barium carbonate, 8 parts charcoal or coke, and 11 parts pitch. The addition of alkalis is not of much use. This mixture is formed into briquettes, which it is necessary to heat in a reducing flame till the pitch is coked, and the barium carbonate converted partially or completely into oxide. The briquettes may be broken up into small lumps, and such lumps may also be formed by heating the mixture of barium carbonate or carbon on the hearth of a reverberatory furnace or in a revolving furnace by means of a reducing flame until the mass is fritted, when it is discharged and broken up into lumps.

These lumps or briquettes are charged into kilns arranged in the manner of an annular kiln, so that some of the chambers are being heated while others are cooling down or are being filled or emptied. A gaseous mixture, as rich as possible in nitrogen, and containing little carbonic acid, oxygen, and aqueous vapour, heated to a temperature of about 1400° C., is passed into the

* No. 103037; Bull. Soc. Chim. vol. xxvi. p. 46.

chambers filled with briquettes, until a sufficient formation of cyanogen compounds has taken place. When this is the case, the stream of heated gas is shut off, and cold gas of the same or similar composition conducted into the mass until the temperature has fallen to 500° C. If the aim be to produce ammonia, the stream of gas is now suspended, and the material treated with steam; hereby ammonia results, is aspirated off and absorbed or condensed. If, however, the aim be to produce cyanogen compounds, the mixture in the chamber must be cooled to at least 300° C. At this temperature it may then be safely removed, lixiviated with water, and the cyanogen compounds obtained from the solution in the usual manner. In order to obtain ammonia, the mass is treated with steam or a fine spray of water at a temperature of 300° to 500°. The lumps thus treated may repeatedly undergo the same treatment, until most of the carbon is consumed. As sources of nitrogen, the gases evolved from the carbonic-acid absorption-apparatus of the ammonia-soda process, and the gaseous mixture obtained by the combustion of coal or coke with the smallest possible quantity of hot air, are the most profitable; and the requisite temperature is most readily obtained by means of a Siemens recuperator, applying this also to the previous heating of the air employed for the combustion. The gases leaving the last chamber which is being heated at the time must be further cooled down by passing them under a boiler or pan, or through a washing-apparatus, before they get into the chamber where the material is just cooling. After having fulfilled this object, these gases, which contain much carbon monoxide, may be burned and used as a source of heat; for instance, for heating air, generating steam, and for other purposes.

For work upon a moderate scale, the following process and plant are recommended. In a heating-chamber B (figs. 139 and 140) stand four ranks of earthen retorts A. Into this combustion-chamber, heating-gas and air, previously heated in a recuperator, enter by the slits *c*, the products of combustion being forced by the wall *a* to surround the retorts and thoroughly circulate before passing to the recuperator R. The lower divisions H of the retorts A are made of iron, and are either surrounded by water or are kept constantly sprayed by means of the jets *e*. The tubes D serve to introduce the gases rich in nitrogen into the cooling-chambers H, and by the tubes *d*

Fig. 139.

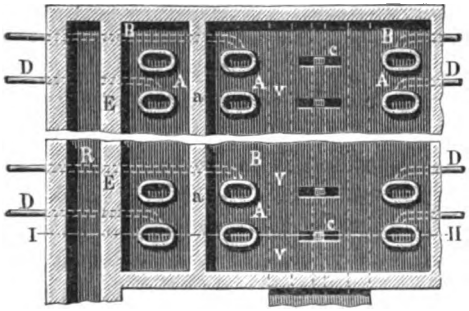
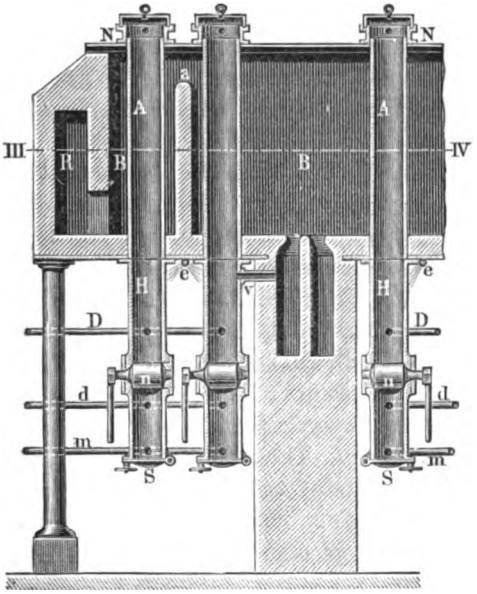


Fig. 140.



the passage of steam is effected. The retorts A having been charged with the briquettes, the temperature is raised to 1100–1400° C., and nitrogen passed in through D, traversing the mass in H and abstracting heat therefrom. From time to time *n* is closed and portions of the product are removed by the door S, new briquettes being fed in at N. For the conversion of the resulting cyanogen compounds the masses taken out of H at a temperature

of 300° may be treated in a separate apparatus; or, more simply, the cock *n* is closed, and through the subjacent mass, still at a temperature of 500°, steam is passed by means of the tube *d*, the ammonia formed issuing at *m*. When the formation of ammonia has ceased, the portion of the retort below the cock *n* is emptied; the cock is opened in order to fill that space again, and a fresh charge of briquettes is introduced at the top of A. In some cases it will be found advantageous to use hot generator-gas instead of a cold gaseous mixture containing nitrogen. Requiring less heat from B, the work done by the retorts will be hereby increased, but the cooling-space H will require to be enlarged, since it is only cooled from without. But the cooling within the space H may also be hastened by passing in cold gases at D, and at the same time hot generator-gases at *v*. In that case an opening must be provided in the upper part of H just below *v*, by which the greater part of the cooling gases may escape; and it is best to provide a cock or slide between these two parts. The gases which leave the retorts A, being rich in carbon monoxide, may be utilized for heating purposes.

Mond's process, although tried on a somewhat large scale, has not yet come into practical operation, and is therefore probably at this moment not yet worked out so as to be fully successful.

Another development of the same method has been attempted by L. Q. Brin and A. Brin (B. P. 3089, 1883), combining with it the manufacture of barium peroxide, according to their patent No. 1416 of 1880 (G. P. 15298). There are two sets of retorts. One of them contains barium oxide, which is kept at a temperature of 600°, and retains the oxygen of the air passed in, with formation of barium peroxide. The remaining pure nitrogen is pumped over into the second set of retorts, charged with "barytic coke," at a temperature of 800°. The barytic coke is made from equal parts of barium oxide or carbonate and charcoal powder, agglomerated by coal-tar. Thus the barium is completely transformed into cyanide, which is converted into NH_3, CO_2, and BaO by passing in steam at a temperature of 300°. The second set of retorts is heated with generator-gas, and the surplus heat of the fire-gases serves for heating the first set of retorts.

J. Young (B. P. 16046, of 1885) recommends as a suitable material for retorts, destined for manufacturing cyanogen compounds by the above described processes, non-acid and non-

metallic substances. Compressed coke or plumbago answers moderately well; but magnesian limestone is the best. The raw limestone is calcined, ground, mixed with tar, moulded and re-burned, exactly as is done for bricks for use in the Thomas-Gilchrist dephosphorizing process. [It is more than doubtful whether such retorts would stand the wear and tear of the process, and a "basic" material does not seem to be called for in this case, as the baryta mixture does not fuse.]

Another modification of the above principle is that patented by T. B. Fogarty (B. P. 5361, 1883). He leads ordinary producer-gas, freed from moisture and in a high state of incandescence, downwards through a tower in which a shower of intimately mixed and finely comminuted carbon and alkali is constantly falling. At the bottom of the tower is a pit containing water to catch the falling material, provided with an opening for the escape of the gas. A great deal of the nitrogen of the producer-gas is taken up by the carbon and alkali to form alkaline cyanides, which are met in their downward course by a steam-jet introduced into the lower part of the tower. Thus the cyanogen compounds are decomposed, ammonia being formed, which is then washed out by scrubbers. The gas left after this treatment is next conducted into a retort where ordinary bituminous coal mixed with alkali is undergoing distillation. Here a further combination of nitrogen with carbon and alkali takes place, with formation of cyanogen compounds. Some of these are decomposed by the aqueous vapour in the retorts, but the bulk remains in the coal left behind in the retorts. The producer-gas here serves as a diluent or absorbent of the rich hydrocarbon vapours which are given off by the coal in the early stage of the distillation, and which would otherwise be converted into tar. After leaving the retorts, the gases are again scrubbed for ammonia. After the distillation is over, the coke is brought, with as little exposure to the air as possible, into a closed vessel, where a stream of water is allowed to play upon it from the top. The steam thus generated decomposes the cyanides with evolution of ammonia, which passes upwards through the new cool layers of coke above, and with the gases generated simultaneously is led away and recovered by scrubbing.

D. Ammonia formed in Inorganic Chemical Manufactures.

In some cases, where nitrate of soda is used for oxidizing pur-

poses, ammonia is formed, and proposals have been made for its utilization. This is, for instance, the case with the ammonia formed in very perceptible quantities during the oxidation of the sulphur compounds in the manufacture of caustic soda*. It would seem very difficult to recover this slight quantity of NH_3 dispersed in an enormous volume of other gases. But at the Aussig Chemical Works this is actually done; and in 1884, 60 tons of ammonium sulphate were obtained from this source.

E. Ammonia from Urine, Sewage, and other Animal Secretions.

Urine is no doubt the oldest source of ammoniacal compounds, and up to a comparatively recent period it has been practically the only one for manufacturing purposes. The oldest chemist who really deserved that name, the Arabian Geber, who lived in the eighth century, undoubtedly prepared sal-ammoniac from urine and common salt. Sal-ammoniac, made in this way, was an article of commerce in Europe as early as 1410; and the Jesuit Sicard in 1720 describes a manufactory of it in the Delta of the Nile which he had visited. In Egypt sal-ammoniac was made by mixing camels' dung with salt, burning it, and collecting the sublimate; we shall give some more particulars about this in the section "Sal-ammoniac" in Chapter XIV.

Putrefied urine (in which the urea has passed over into ammonium carbonate) has been used for centuries, and to a certain extent is still used by dyers as a source of ammonia for scouring wool and other purposes.

The methodical collection of urine or sewage and working it up into ammoniacal compounds has been carried out in the neighbourhood of some large towns, *e. g.* Paris; but this industry represents only a very small proportion of the enormous quantity of animal ejections passing off in other ways, and it furnishes only a comparatively small fraction of the ammoniacal compounds required in trade. If all the ammonia corresponding to London urine were recovered, this would amount to the enormous total of more than 60,000 tons of sulphate per annum.

Normal urine contains from 20 to 35 grams urea per litre:

* Comp. especially Lunge and Smith, Journ. Soc. Chem. Ind. 1883, pp. 460 and 525.

an adult man produces from 22 to 37 grams urea per 24 hours, along with $\frac{1}{30}$ to $\frac{1}{60}$ of that weight of uric acid; this corresponds to 12·5–21 grams NH_3 per day, or between 9 and 17 lb. per annum. Urine, left to itself, after a short time enters into a sort of fermentation, the result of which is, that urea, or carbamide, $CO(NH_2)_2$, is changed into ammonium carbonate, $(NH_4)_2CO_3$, under the influence of a microscopic fungus.

In Paris* there are daily 2200 cubic metres (say, tons) of urine and night-soil taken out of the "fosses," partly disinfected by sulphate of iron or zinc, and are left to settle in large reservoirs, where the solid matters separate from the liquid sewage, forming 85–95 per cent., which is now called "eau vanne." In three or four weeks the fermentation is complete; the urea has vanished, and there has been formed principally ammonium carbonate, along with sulphhydrate, sulphate, chloride, ammonio-magnesian phosphate, compound ammonias, and other substances of intensely disagreeable smell. There is always a considerable loss of nitrogen, partly as such, partly by the evaporation of ammonia, and partly by its oxidation into nitric acid. At the end of the fermentation the clear "eau vanne" is drawn off from the muddy deposit, which is converted into manure, but always with much loss and causing a great nuisance.

Several processes have been introduced for treating this very disagreeable deposit, of which we will give an outline. The Bilange process, practised at Bondy, is applied to the whole of the sewage. This is mixed by mechanical agitators with an exactly measured quantity of chemicals, intended to favour a rapid settling, principally consisting of milk of lime of specific gravity 1·16–1·20. The mixture is allowed to settle in tanks, holding 500 tons each. After an hour the clear liquid is pumped away; it has an amber colour and contains free ammonia. The albuminoid matters are precipitated along with carbonate of lime and most impurities. The decanted liquid is replaced by a fresh mixture from the agitators; the clear portion is again decanted, and this is continued until the tank is full of deposit. The thick mud is now heated by steam (it is more easily pressed in this state) and is passed through filter-presses. The ammonia escaping during the heating is retained in tanks filled with sulphuric acid. The cakes turned out from the

* C. Vincent, "Industrie des produits ammoniacaux," Enc. chim. Frémy, 2nd section, 10th vol. 4th part, p. 7.

filter-press are much richer in nitrogen the less lime has been used. Each 100 cubic metres of crude sewage yield 75 cubic metres clear decanted liquid and 25 cubic metres deposited mud, from which is obtained 6 or 7 tons of cakes at 50 per cent. moisture. The manurial value of the latter is very small. The liquid is worked up in the ammonia-stills.

The Kuentz process is worked in several places, *e. g.* at Versailles. The crude sewage is received in closed tanks, where it passes through zigzag channels, and thus undergoes a first settling. The clear liquid issuing at last is sent to the ammonia-stills. The thick deposit is pumped into a closed mixer, where it receives an addition of the chlorides of aluminium and iron and of phosphate of lime, in order to make it pass through the filter-press and enhance its manurial value. The reagent is prepared by treating a mixture of 15 parts bauxite, 75 parts natural phosphate of lime, and 3 parts hydrated oxide of iron (yellow hematite), with 110 commercial hydrochloric acid and 150 water. 50 kilog. (1 cwt.) of the liquid resulting from the reaction is added to each cubic metre of thick mud. After 24 hours' settling a considerable quantity of clear liquid, of only a faint smell, has collected at the top and is decanted, and the deposit is forced by compressed air into a filter-press. The cakes contain all the phosphoric acid as bicalcic phosphate, precipitated by the ammonium carbonate, along with calcium carbonate; the iron has absorbed the sulphur compounds, and the alumina has modified the albuminous and slimy matters which otherwise would have impeded the filtration. The percentage of nitrogen in these cakes is 3–3·5, that of assimilable phosphoric acid 10–12 per cent.

The ammonia-stills must be specially adapted to avoid the smell inherent to such matters; they will be described in the last chapter.

It is hardly necessary to observe that all such processes only apply to concentrated night-soil, not to sewage diluted with a large quantity of water from water-closets &c.

We will now enumerate the more recent patents referring to this subject.

J. P. Rickman and J. B. Thompson (B. P. 3305, 1882) add to urine and night-soil putrefying ox-gall as a ferment. The upper space of the closed tank in which the mass is kept is connected with a reservoir containing sulphuric acid, to absorb the ammonia

escaping. The liquid remaining in the fermenting-tank is afterwards distilled at a low temperature; the vapours from the directly heated still first pass through liquid contained in a cold still and thence into the absorbing-vessels.

J. Young (B. P. 3562, 1882; G. P. 27034) distils off a portion of the sewage, or of the effluent waters of sugar manufactories, either by itself or mixed with lime, at a pressure above or at or below that of the atmosphere; the distillate contains a greater proportion of ammonia than the original sewage. His apparatus consists of a series of long boxes, arranged like steps, and provided with false bottoms inclined in such a way that when the boxes are filled with the liquid, which is previously warmed and mixed with lime, the steam which is admitted at the bottom can be sucked by means of a vacuum backwards and forwards through the whole battery of boxes, while fresh liquid flows continuously in at the top and out at the bottom. Instead of the boxes, cylinders may also be employed.

J. Duncan (G. P. 27148 and 28436) treats sewage, mixed with lime and cleared by settling, with steam in such a manner that the boiling-point 30° C. is never exceeded. This is done by means of a series of vessels combined into a battery, in which the liquid travels in the opposite way to the steam. When the liquid contains only about 0·5 gram NH_3 per litre, steam takes up hardly more than $\frac{1}{800}$ of its weight of NH_3 in a vacuum in which water boils at 21° C. It is therefore best to take the ammonia out of the steam by sulphuric acid, and employ the "purified" steam over again (?).

F. J. Bolton and J. A. Wanklyn (G. P. 17386) pass the vapours from heated sewage &c., mixed with air or carbonic acid, through layers of porous calcium sulphate, mixed or not with calcium and iron phosphate, of calcium chloride, of its double salts with potassium or sodium chloride, or of potassium-magnesium chloride. The ammonium carbonate is transformed with those reagents into calcium carbonate and ammonium sulphate or chloride. When the reaction has gone far enough the mixture is heated, whereupon the inverse reaction takes place; ammonium carbonate escapes [of course in a dissociated form], and the original salts remain to be used over again.

C. H. Schnieder (G. P. 27671 and 32890) promotes the natural settling of sewage by the addition of calcium chloride, whereby

the ammonia is converted into a non-volatilizing compound; the slimy matters are also precipitated, and with old sewage a clear liquid is obtained which is easily decanted. With fresh sewage a further clarification by aluminium sulphate is advisable.

Richters and Hagen (G. P. 14210) force air into the mixture of sewage or night-soil with lime, by means of perforated pipes, and condense the ammonia in coke-scrubbers by sulphuric acid.

Brullé and Leclerc (B. P. 1086, 1880) run the sewage &c. in thin layers over heated surfaces, and cause a current of air, passed over those surfaces, to carry away the ammonia.

I. van Ruymbecke (Am. P. 342237, of 1886) seeks to submit liquids containing organic substances to a rapid putrefying process, by allowing them to act in the shape of a spray on substances impregnated with putrefaction-ferments in the presence of a strong current of air, so that air, ferment, and liquid are brought into intimate contact. The escaping air is deprived of its ammonia by treatment with sulphuric acid, and the residual liquid is also treated for ammonia as usual.

Buhl and Keller (G. P. 27671) precipitate the phosphates with lime salts and crude manganese chloride (still-liquors from the manufacture of chlorine); the settled liquor is distilled for ammonia. This process is at work at Freiburg in Baden, and is stated to give a very good yield of ammonia.

F. Ammonia from Guano.

Apart from the deposits of ammonium bicarbonate sometimes found in Peruvian guano (p. 517), it is possible to extract considerable quantities of ammonia from guano by heating it with lime. This process was patented by Young in 1841; but it cannot be remunerative, since the direct manurial value of guano is superior to that of the ammonia salts obtainable therefrom.

G. Ammonia from Bones, Horn, Leather, Wool, Hair, and other Animal Substances.

The carbonization of *bones* is carried on on a large scale for the manufacture of bone-charcoal, a substance very largely used in sugar manufactories and for several other purposes. In Germany and France this is generally done by heating the bones in iron

pots, one on top of another, which are placed in large numbers in a furnace, heated by a fireplace built on one side of it. Thus the gases proceeding from the fireplace get mixed with those escaping from the carbonizing bones, and the ammonia contained in the latter is too dilute to be condensed; but there is also too little of it to begin with, as the temperature in this case is very high and most of the ammonia is destroyed (Chap. XIII.).

In England and Scotland bone-charcoal is generally made by heating the bones in iron or fireclay retorts, provided with condensing-apparatus similar to that of gas-works. In these a kind of tar, called "Dippel's oil," and some ammoniacal liquor are collected. This tar consists to a great extent of pyridine derivatives, and has found next to no use so far, but it may in the future become a very important starting material for the manufacture of artificial alkaloids and of some colouring-matters. The ammoniacal liquor is worked up exactly like that of the ordinary gas-works; it is probably more contaminated than the latter with pyridine bases.

The proportion of ammonia formed in this case is much larger than when charring the bones in pots, as in the former case the gases are subjected to cooling immediately after leaving the retorts, while in the latter case they are exposed to the full heat of the fire-gases and the ammonia is thus decomposed. Moreover, the temperature attained in the retorts is lower than that in the pots, and that is precisely the reason why many continental manufacturers prefer the latter system, as the bone-char is thus of better quality.

The bones intended to be charred must be first freed from fleshy particles &c., by steeping in water (preferably tepid) for 24 hours, and mechanical cleaning; they are then roughly broken up by fluted rolls and are submitted to the process of removing the grease. This formerly always consisted in boiling them in water, preferably in a butt or pan, heated by a steam-coil, in which the bones are suspended in wire-work baskets; after a few hours' boiling, all the grease is found floating on the top, and is carefully ladled off, after which the baskets holding the bones are lifted out, the bones are then thoroughly washed, and at last dried by prolonged exposure to the air. Recently several processes have been introduced for removing the grease by washing with bisulphide of carbon, benzoline, and the like, in specially

constructed closed apparatus, which admit of recovering the solvent, but which cannot be described here.

The dried bones are sometimes at once submitted to the charring process, especially when this takes place in retorts; but where they are to be charred in pots, they are usually first broken up by studded or fluted rolls, and the pieces sorted by machinery, so that the different sizes required by the consumers of bone-char are obtained beforehand. The smaller particles, which are of very little value as char, are ground up into bone-dust for manure; the rougher ones are separately charred.

The retorts for charring bones are sometimes horizontal, of a section similar to gas-retorts, and are fired in the same way; sometimes they are, however, perpendicular, and in that case they can be worked continuously, part of the contents being from time to time withdrawn at the bottom, and cooled without contact with air, while fresh bones are being introduced at the top. The gases are conveyed away by a lateral tube near the top, and are first passed through a hydraulic main, or some similar-apparatus, where they have first to traverse a shallow layer of water; they then pass through a cooling-apparatus, which may consist of a series of upright metal pipes, connected alternately at top and bottom, and cooled by air or by a water-spray, and afterwards through an ordinary scrubber. The remaining gases, which still possess a very disagreeable smell, are conveyed back into the retort-fire and are burnt there. Care must be taken to introduce them in a very hot place, so that the combustion may be complete. Of course it is preferable to promote the passage of the gases by an injector or exhauster.

The condensing liquids are allowed to settle in tanks where the tar (Dippel's oil) is separated; it amounts to 1·7–2 per cent. of the weight of the bones, and up to the present it is mostly burned as fuel under the retorts. The ammoniacal liquor is worked up like gas-liquor, as will be shown in the 14th chapter; it generally yields from 6 to 7 per cent. of ammonium sulphate of the weight of the bones, of somewhat inferior quality and strongly coloured. (If all the nitrogen contained in the bones were converted into ammonia, this would amount to 20 or 25 per cent. of sulphate.)

A process sometimes followed in France consists in filtering the crude ammoniacal liquor through a layer of plaster of Paris (sulphate of lime); the ammonium carbonate is thus transformed into

sulphate, which is recovered by evaporation, insoluble carbonate of lime remaining on the filter.

H. P. Lorenzen (G. P. 9989) passes the gases evolved in charring bones over red-hot lime, where the tarry matters are burned, and condenses the ammonia in coke-scrubbers charged with dilute sulphuric acid.

H. J. and E. B. Castner (B. P. 4057, 1882) also carry the products of the continuous distillation of bones, along with air, through heated tubes, and thence over hydrate of lime, and after cooling into sulphuric acid. [The addition of air and subsequent heating would tend to destroy much ammonia.]

Other animal refuse (wool, hair, skin, horns, feathers, sponges, leather, and so forth) is principally employed for two purposes, namely for manufacturing prussiate of potash and for manure. In the former case the refuse matter is sometimes charged directly, or after being simply dried, into melted carbonate of potash, and in this case of course no ammonia can be recovered. But sometimes the animal matters are first charred in retorts, exactly as has been described in the case of bones, and the ammonia formed is recovered in the same way. It has been found that the charred matters yield the same quantity of cyanogen compounds as if they had been employed in the raw state, that is at most one fifth of the quantity corresponding to their percentage of nitrogen (say 10 to 15 per cent.). Hence all the ammonia recovered in the charring process would seem to be a clear gain; but in spite of this not much is made in that way, as the expense of charring in retorts in any case swallows up most of the profit. 1000 parts of horn on carbonizing furnishes, according to Dumas, 500 parts of ammoniacal liquor at 8–10° Tw. and 160 parts of Dippel's oil. Some of the ammonia can be obtained as a solid sublimate of crude ammonium carbonate.

The utilization of these refuse animal matters for manurial purposes takes place in different ways. Sometimes they are exposed to the action of steam in closed cylinders, whereupon they become friable and are then ground up and mixed with superphosphate, &c. Sometimes they are added without any preparation to manures otherwise prepared, but in that case they desintegrate in the soil with extreme slowness. The most successful treatment of these substances seems to be: dissolving them in hot concentrated sulphuric

acid (which can be performed in cast-iron vessels), and utilizing that acid for manufacturing superphosphate. In this case most, if not all, the nitrogen is converted into ammonia, as is done in Kjeldahl's analytical process for determining the percentage of nitrogen. But this ammonia is, of course, never separated in the free state or in the shape of a salt, being at once incorporated with the other parts forming the chemical manure.

Another process admits of recovering the ammonia as such, and is also, as it were, based upon an extremely well-known analytical process, namely the estimation of nitrogen by soda-lime. L'Hôte treats the refuse matters with a 10-per-cent. solution of caustic soda, in the cold or at such a moderate temperature that no ammonia is set free. The matters are thus converted into a pulp or completely dissolved. This pulp or liquid is mixed with slaked lime and the solid mass is charged into cast-iron retorts, where it is heated at first only gently, to avoid a destruction of ammonia, afterwards to a red heat. The ammonia contained in the escaping gases is condensed by means of sulphuric acid. The residue is composed of sodium carbonate and lime, and when treated with water regenerates the caustic soda [no doubt only imperfectly], which can be used over again.

H. Proschwitzky (G. P. 10957) charges retorts with alternate layers of one part of refuse leather and four parts of lime. The gases evolved by heating are first passed through condensing-apparatus for separating tar, ammoniacal liquor, and crude ammonium carbonate, and thence into sulphuric acid. The remaining mixture of charred leather and lime is to serve as manure. The uncondensed gases are used for heating the retorts.

Th. Richters (G. P. 13594) soaks leather, blood, wool, hair, and other animal refuse with a solution of carbonate of potash, dries the mass, and heats it in retorts, without proceeding to fusion. The volatile products ammonia, tar, and gas are treated in the usual manner. The residue contains potassium cyanide, cyanate, sulphocyanide, carbonate, hydrate, sulphide, and carbon. It is lixiviated with water in the presence of metallic iron or ferric hydroxide; thus the potassium cyanide is converted into ferrocyanide (prussiate of potash), which is recovered by crystallization; the mother liquor is used again for treating animal matters, and the caustic potash contained therein is converted into carbonate by admitting carbonic acid during the drying process. [An alto-

gether similar process for the simultaneous manufacture of prussiate of potash and ammonia was tried, as early as 1860–62, by me, in company with another chemist, on a practical scale, and some tons of both products were manufactured; but the process was given up on account of the difficulty of preventing the mass from fusing in the retorts, which made its discharge a very awkward operation and rapidly destroyed the retorts. It is, however, possible that these technical difficulties might be overcome. The ammonia is, of course, quite a secondary product in this case, the value of the prussiate of potash being far greater.]

W. H. Marriott (B. P. 4369, 1881) distils animal refuse in a kiln by introducing at the bottom a mixture of producer-gas and of the exact quantity of air necessary to burn it. [No doubt the temperature is much too high to be favourable to the formation of ammonia.]

H. Ammonia as a By-product in the Manufacture of Beet-root Sugar.

Beet-root contains betaine (trimethyl-glycocoll)

$$(CH_3)_3N\begin{matrix}-CH_2-CO-\\ -O-\end{matrix}\Big],$$

asparagin $CH_2(NH_2)-COOH$
$\quad\quad\quad

off the alcohol. The best-known process is that of Cam. Vincent*, which has for its principal object the manufacture of trimethylamine and methylic chloride, but considerable quantities of ammonia are obtained at the same time (about 32 cwt. of ammonium sulphate from 98 tons of molasses, or 400 tons of vinasse, treated per diem). The evaporated vinasse is ignited in retorts and the gases submitted to condensation; the tarry liquid which separates is saturated by an acid and evaporated to a certain degree; on cooling, the ammonia salts, which are less soluble than the others, crystallize out. A further quantity of ammonia is obtained in the dry distillation of the trimethylamine hydrochlorate, in a similar way to the above. The ammonium salt thus obtained (generally the hydrochlorate) is much contaminated with the chlorides of iron and lead from the metal of the vessels; it is purified by dissolving in water, adding ammonium sulphide, filtering, crystallizing, and draining the crystals in a centrifugal machine.

E. Ernst (G. P. 13871) mixes with the vinasse, concentrated to 76° Tw. and still hot, 25 per cent. dried ground peat, 3 per cent. ground quicklime, and 6 per cent. fatty oil. The mixture is charged into a semicircular piece of sheet-iron, which is placed in a red-hot horizontal retort, iron rails preventing a direct contact between the sheet-iron and the retort-shell. The gases formed are treated as usual. Further patents of the same inventor (G. P. 17869 and 18549) describe other arrangements for igniting mixtures of vinasses with peat &c.

R. Lederer and W. Gintl (G. P. 17874) calcine the concentrated vinasse in a continuous stream, at a temperature of 350–400° C., in a horizontal retort, fitted with an Archimedian screw, so that the char continuously issues at the other end, ready for the recovery of potash salts, the gases being treated by Vincent's process.

F. X. Brosche (G. P. 14433) believes that 60 or 70 per cent. of the nitrogen of the vinasse can be recovered as ammonia by dry distillation of the vinasse over potash-lime, formed by a mixture of carbonized vinasse with lime. Up to 80 per cent. is obtained if the vapours are, moreover, passed through a tube filled with potash-lime.

The Badische Gesellschaft für Zuckerfabrikation (G. P. 15702)

* Compt. Rend. 1877, 21 mai and 8 octobre.

extracts carbonized vinasse with water, causticizes the solution by lime, evaporates the liquor, and adds so much of it to concentrated vinasse that there is from 5 to 15 parts of potassium hydrate present for each 100 parts of dry vinasse. The dry distillation is then carried on as usual.

Haring, Ehrenberg, & Co., and M. Baswitz (G. P. 15751) introduce concentrated vinasse, or the liquors from the osmose and elutriation processes, in a very thin stream into retorts heated to a dark red heat, so that there is almost instantaneous gasification. The gases, which are very rich in tarry matters, are subjected to overheating in pipes placed between the retorts, where the tar is destroyed [along with some of the ammonia?], and thence pass into the condensing-apparatus.

Even from the *potash* made from vinasse, which contains some potassium cyanide, Legrand and Dabernard (Fr. P., Dec. 27, 1876) believe that they can obtain ammonia by treating it with steam. Thus 1 to 4 per cent. ammonium sulphate is to be obtained from potash. [This will hardly pay!]

In treating molasses with lime and alcohol, for the purpose of recovering the sugar, the alcohol distilled off from the calcium saccharate contains ammonia. H. Steffens (G. P. 23594 and 24549) treats it with sulphuric, carbonic, sulphurous, or phosphoric acid, or acid salts, in order to recover the ammonia. Another process is that of R. Schiller, G. P. 38596.

If all the beetroot-sugar works in Germany were able to recover the total ammonia given off during the manufacture, it would amount to 15,000 tons of sulphate per annum.

I. Ammonia from Peat.

Peat contains a very considerable quantity of nitrogenous compounds, most of it probably already in the form of ammonium salts, partly formed by the decomposition of organic matter, and partly absorbed from the atmospheric air. The nitrogen found in it sometimes amounts to 4 per cent., and by dry distillation the best descriptions of peat yield up to 8 per cent. by weight of ammonium sulphate; even inferior qualities yield about half that amount.

The dry distillation of peat further yields a tar very rich in phenols, acetic acid, and paraffin, and it has been worked for the

latter products in some parts of Germany and France, but is now probably quite superseded for this purpose by richer materials, as bituminous lignite, shale, &c. The cessation of this industry involved also that of the recovery of ammonia by the same process.

Sometimes peat has been treated in specially constructed gas-producers, where the ammonia is washed out from the gas before using the latter for heating purposes. Such a "gazogène distillateur," constructed by Lencauchez, is described and figured in C. Vincent's 'Industrie des produits ammoniacaux,' p. 82; but the recovery of ammonia in that case must proceed on the same lines as that proposed for gas-producers in general (see later on, under L), and is equally unremunerative in most cases.

H. Grouven has made a special study of the recovery of ammonia from peat, especially that obtained from certain kinds of moor-lands ("Bruchmoore" and "Grünlandmoore"), which sometimes contains up to 3·8 per cent. N. The principle of Grouven's process (G. P. 2709, 13718, 18051) is, mixing the damp peat with chalk (in order to fix the sulphur), heating this mixture in upright cylinders by means of the gases remaining from the subsequent stages of the process, and passing the gaseous products of this dry distillation through a "contact substance," consisting of peat, chalk, and clay in equal proportions, moulded into the shape of drain-tiles, and heated in upright cylinders to a proper temperature. Here the nitrogen, under the influence of the incandescent aqueous vapour, hydrocarbons, and hydrogen given off in the first cylinders, is, to a great extent, converted into ammonium carbonate, which is condensed by calcium sulphate (p. 534), and thus converted into ammonium sulphate, or else by strontium sulphate (G. P. No. 34086).

Grouven's process was taken up by a company, and prolonged experiments on a large scale were made with it, but without pecuniary success, in spite of the then high price of ammonia. The question of utilizing the very large quantity of nitrogen contained in peat is therefore not yet finally solved, as it would not stand competition with the processes where ammonia is a by-product.

K. Ammonia from Bituminous Shale.

The distillation of bituminous shale, for the purpose of obtaining oils and paraffin, is a very important industry, and has attained very large proportions, especially in Scotland, where a suitable

raw material is abundant. In converting the oils, ammoniacal liquor is also obtained. Many of the processes latterly proposed for recovery of ammonia from coal (see under L) equally apply to bituminous shale, and need not be described here. We here mention only the patent of Playfair (B. P. 3977, 1882), who mixes with the shale, before introducing it into retorts, an alkali or alkaline earth, for the purpose of increasing the proportion of nitrogen given off as ammonia; and that of A. Neilson and J. Snodgrass (B. P. 4902, 1885), who, after having worked off the whole or nearly the whole of the oil in the ordinary way, either in horizontal, or vertical, or inclined retorts, introduce a mixture of air and steam, all external heating being discontinued. The air burns the carbonaceous matter remaining in the retort, and the increased heat causes the evolution of a large amount of ammonia in addition to that obtained in the primary distillation.

L. Ammonia from Coal.

Quite apart from the nitrogen forming four fifths of our atmosphere there is an enormous quantity of nitrogen existing in the form of organic substance and of products emanating from its decomposition. But for all practical purposes this is not of any great importance as a source of ammonia compounds in comparison with *coal*. Although only a small proportion of the nitrogen of coal is utilized in the shape of ammonia, nearly the whole of our requirements are supplied from this source.

The quantity of nitrogen in coal is very much greater than that contained in the fresh vegetable matter which forms the original material of coal. Such vegetable matter rarely contains more than 0·1 per cent. N, whilst in coal we find from 10 to 20 times as much. This excess of nitrogen may have been partly absorbed from the atmosphere in the shape of ammonia (p. 539), but in all probability much of it represents the remains of the animals which lived during the growth of the coal-forming forests or swamps; just as we must attribute the same origin to the nitrogenous substances contained in bituminous shales.

The amount of nitrogen in coal varies from about 1 to 2 per cent. According to Dr. C. Meymott Tidy (communication to the Author), coal contains:—

From Wales	0·91	per cent. N.
From Lancashire	1·25	,,
From Newcastle	1·32	,,
From Scotland	1·44	,,

W. Forster* found:—

From Welsh anthracite	0·91	per cent. N.
From English coal	1·66 to 1·75	,,
From Scotch cannel	1·28	,,

Only a small proportion of the nitrogen contained in coal is utilized in the shape of ammonia. More than 90 per cent. of the coal consumed in this and other countries is used in such a way that the recovery of ammonia from the products of combustion is nearly or altogether impossible; and of the remaining 10 per cent., only that portion is really fully utilized for the production of ammonia from which coal-gas is manufactured; while the recovery of ammonia from coke-ovens &c., about which more will be said hereafter, is still in its infancy. Thus up to the present nearly the whole of the ammonia found in trade is a by-product of the manufacture of coal-gas; and this will also be the case in future so long as the demand for ammonia does not exceed the supply from that source. That emergency seemed to arise at one time; and in consequence of this it was at once proved that a further enormous source of ammonia was present in the method of carbonizing coal which is practised in the production of coke for metallurgical purposes. The progress in this direction has not been very rapid, because of the quick subsidence of the price of ammonia, which by itself proves that the demand does not as yet exceed the supply. As soon as that is the case, coke-ovens will be undoubtedly generally reconstructed for the recovery of ammonia as well as of coal-tar, which is always formed at the same time as the former, and of which we have treated at length in Chapter II. Only when this second source of ammonia has been drawn upon to a large extent will it become probable that the further means for increasing the production of ammonia, as described in this chapter, will be turned to profitable account. But the utilization of the nitrogen even from coal which is burnt for

* Proc. Inst. Civil Eng. lxxvii. part iii. p. 23.

household purposes and for raising steam, as is often thought of or spoken about, seems to be a matter of the remotest future; and it is less necessary to consider in this place, as not the slightest *practical* idea has yet been thrown out as to how this could be done. Nearly the whole of the nitrogen of the coal actually *burned* escapes in the elementary form, the temperature being much too high for the formation and existence of ammonia. We can only hope to obtain any considerable amount of ammonia when coal is not properly burned, but submitted to *dry distillation*, as in gas and coke making, or by special agencies of which we shall speak later on, but which as yet have found no profitable application.

It is true that it would be a great boon for agriculture if ammonia could be supplied for manurial purposes at a much lower figure than has hitherto been done. At present the major part of the nitrogen contained in chemical manures is the native nitrate of soda, which comes to us exclusively from Chili, and of which it is computed that about 300,000 tons annually are used for agricultural purposes. As nitrate of soda contains 16 per cent. N, the above quantity is equal to 48,000 tons of nitrogen. Taking the present annual production of coal in the whole world at 360 millions of tons, and its average percentage of nitrogen = 1·33, we find the nitrogen of the coal now consumed per annum to be = 4,800,000 tons, or just 100 times as much as that of the nitrate of soda consumed as manure *. Hence it would be sufficient to recover only one hundredth part of the nitrogen of coals, in the shape of ammonia, to replace all the nitrate of soda used in agriculture.

If the manurial value of nitrate of soda and of sulphate of ammonia were exactly in the proportion of their percentage of nitrogen, 100 parts of the former would be equivalent to 78 parts of the latter. But the actual prices obtained in commerce do not correspond to this. Bunte † has discussed this question at length. He urges that, as a manure, nitrate of soda is certainly much more rapid and active, but ammonium sulphate, if slower, is more durable, and that the latter is not, like the former, washed out by the rain, and hence should be much more economical than nitrate in the

* Cl. Winkler, Jahrb. f. Berg- u. Hüttenwesen in Sachsen, 1884.

† Schilling's Journal f. Gasbeleuchtung und Wasserversorgung, 1885.

long run. This seems to be borne out by the fact that the price of nitrogen in the shape of ammonia is nearly always higher than that in the shape of nitrate of soda, in the proportion of about 17 to 15. The annual importations in Germany were, in :—

	1881.	1882.	1883.	1884.	
Sulphate of ammonia ...	34,652	34,117	27,886	35,966	tons.
Other ammonia salts and liquor ammoniæ	820	783	871	1261	„
Nitrate of soda.....	89,949	126,918	166,184	200,647	„

Even if we add the ammonium sulphate produced in Germany itself, which is reliably estimated as 10,000 tons (the exportation of all these articles is inconsiderable, 899 tons in 1884, 2067 tons in 1885), the total ammonium sulphate consumed in 1884 in Germany did not amount to one quarter of the nitrate of soda consumed, and of that quantity less than one third was produced in Germany itself. Even if the ammonia from all the coal now consumed for gas-making in Germany (about 1,700,000 tons) were utilized, this would only produce 17,000 tons of sulphate, or one half of the quantity imported. But if about one half of the more than 8000 coke-ovens now at work in the provinces of Rhineland and Westphalia alone were converted so as to utilize their by-products, this would cover the 36,000 tons imported in 1884. So far this factor has not yet seriously influenced prices, as the number of coke-ovens constructed for this purpose falls far short of that quoted above (comp. pp. 50 & 74), and at the present prices of ammonia no rapid extension of this process can be expected. But it is quite certain that any rise of prices would at once cause a further extension of the recovery of ammonia and tar from coke-ovens, and that, for this reason, any permanent reaction in favour of higher prices of ammonia seems out of the question.

That the great increase in the consumption of nitrate of soda in Germany is not an isolated phenomenon is proved by the following figures, showing the total exportation of that article from Chili to Europe (Bunte) :—

In 1880	180,000	tons.
1881	280,000	„
1882	410,000	„
1883	500,000	„

The following table shows the annual averages of prices for 11 years, both for sulphate of ammonia and for nitrate of soda, and for the nitrogen contained in these products, taking as the basis ammonium sulphate at 24 per cent. $NH_3 = 19{\cdot}84$ per cent. N, and nitrate at 95·2 per cent. $NaNO_3 = 15{\cdot}6$ per cent. N. The prices are taken from the Liverpool quotations:—

Average prices for 100 kilog., in marks.

Year.	Commercial sulphate of ammonia.		Commercial nitrate of soda.	
		Nitrogen.		Nitrogen.
1874	34·2	173	23·8	152
1875	37·0	187	23·5	150
1876	37·2	188	23·4	149
1877	39·62	200	27·6	176
1878	40·50	205	30·0	192
1879	36·87	186	29·5	189
1880	38·0	192	31·4	201
1881	40·45	204	29·3	188
1882	40·85	206	26·2	168
1883	33·00	167	22·4	143
1884	28·08	142	20·0	128

(If these prices are taken as shillings, they are as nearly as possible correct by putting 100 kilog. = 2 cwt.)

The only exception to the rule of nitrate-nitrogen being cheaper than ammonia-nitrogen was during the years 1879 and 1880, when the war between Chili and Peru greatly interfered with the exportation from those countries.

1. Production of Ammonia in the Manufacture of Coal-gas.

In the dry distillation of coal, as practised at the gas-works, for the main purpose of obtaining illuminating-gas, it is necessary, in order to purify the gas, to subject it to cooling and washing with water ("scrubbing"). In this process two products are obtained from the gas, an oily and an aqueous substance, which, by settling in tanks, separate from each other, and form *tar* and *gas-liquor*. The former has been treated of at length in the preceding part of this book. The latter, which is always obtained along with tar, comes alike from the hydraulic main, the condensers, and

scrubbers, the former, on account of the temperature, being poorer than the latter. Probably in every gas-works all the liquors are united, and either sold or treated in common at the works. Some liquor always remains incorporated with the tar, and is obtained in further settling and distilling it (pp. 195 & 230); but this is comparatively a small quantity, and is generally run to waste by such of the smaller tar-distillers who have not at the same time a contract for gas-liquor.

Some more ammonia condenses in the oxide-of-iron purifiers, and is hence contained in the "spent oxide."

A description of the condensers and scrubbers used at gas-works, of which there is already a very large variety in existence, does not enter within the scope of this treatise, as that matter belongs to gas-making proper. We will, however, mention that by "virgin gas-liquor" is understood to be that which condenses from the gas in the hydraulic main and the air-condensers, and which is sometimes, but rarely, collected by itself, without mixing it with the other liquor obtained in the scrubbers, by washing the gas with water or weak liquor. Generally all the liquor runs into the same tank.

Yield of Ammonia from Coal.

We have seen (p. 541) that coal contains from 1 to 2 per cent. of nitrogen. But in the process of dry distillation nothing like the whole of this nitrogen escapes in the form of ammonia. As early as 1863, A. W. Hofmann stated that coal, in carbonizing, only yields one third of its nitrogen, two thirds remaining in the coke. We cannot wonder at this, if we consider that some of the well-known products of the distillation of coal-tar of the highest boiling-points, as carbazol and its congeners, contain 6 to 8 per cent. of nitrogen. Dr. Tidy remarks that the four descriptions of coal, whose percentage of nitrogen is stated on p. 542, if all their nitrogen reappeared in the gas-liquor, would yield per ton of coal from 142 to 226 gallons of liquor at 4° Tw.; while in practice rarely more than 45 gallons is obtained, usually only 25, in London down to 13 gallons.

W. Foster* showed that, of 100 parts of nitrogen contained in coal, there were obtained, in a laboratory experiment,

* Journ. Chem. Soc. xliii. p. 105.

14·50 parts as ammonia.
1·56 „ as cyanogen.
35·26 „ in the elementary condition (as part of coal-gas).
48·68 „ remaining in the coke.

Watson Smith * found that coal-tar, which Foster neglects in his calculations, contained 1·667 per cent. N (pitch containing 1·595, and coal-tar oils about 2 per cent.); that is, not quite 0·1 per cent. N calculated upon the coal from which the tar is derived. In coke he found:—

Ordinary gas-retort coke	1·375	per cent.	nitrogen.
Bee-hive coke.....	0·511	„	„
Coke from Simon-Carvès ovens	0·384	„	„

This shows that much less nitrogen is driven out of coal in the short process of gas-making than in the long-continued processes of the manufacture of metallurgical coke.

Cl. Winkler (compare p. 543) quotes results of an experiment made in coke-ovens, where 28·7 per cent. of the nitrogen of the coal employed remained in the coke, and 71·3 per cent. escaped with the gases.

The total yield of gas-liquor obtained from various descriptions of coal has been stated (pp. 23–25). It is generally assumed that a production of 20 lb. ammonium sulphate from a ton of coal is a fair yield.

Scheurer-Kestner † points out that the ammonia gained in the coking of coal will only, on the most favourable assumptions (at a price of coal not exceeding 8*s*. per ton), pay for the loss of thermal value suffered in the coking-process; and that, therefore, the proposals for revolutionizing our firing system, by leaving off using coal as fuel directly, and turning it into coke, tar, ammonia, and gaseous fuel ‡, rest on a very unsound basis.

Processes for Increasing the Yield of Ammonia in Gas-making.

1st. *By means of Lime.*—W. J. Cooper (B. P. 5713, 1882) mixes with coal, previous to its distillation, either lime, quicklime, carbo-

* Journ. Chem. Soc. xlv. p. 144.
† Compt. rend. xcvii. p. 179.
‡ Comp. Weldon, p. 82.

nate of lime, or spent lime, the object being to obtain an increased production of ammonia, or of tar or gas. This process has been discussed by J. A. Wanklyn*. It is usually carried out by thoroughly mixing the slaked lime, produced from 2½ parts of quicklime, with 100 parts of coal, before charging this into the retorts. This "limed coal" is stated to yield a slightly larger fraction of its carbon in the form of volatile substances (tar and gas); also to yield a much smaller fraction of its sulphur in volatile forms, and better coke than that ordinarily obtained. In the discussion following Mr. Wanklyn's papers the latter points were seriously contested. It was shown that the retention of sulphur in the coke causes a considerable loss in the value of the spent oxide, and that the quality of the coke is in reality deteriorated. But it cannot be doubted that one point urged by Mr. Wanklyn is correct, namely, that by Cooper's process more nitrogen is converted into ammonia. A number of gas-engineers testified to a substantial gain in ammonia; in one case it was doubled in quantity, the highest yield obtained on the large scale being about 9 lb. of ammonia (= 36 lb. ammonium sulphate) per ton of coal. Whether this gain of ammonia is or is not neutralized by the expense of "liming" and the loss of sulphur in the spent oxide, is a question which must be decided by local circumstances. So far, only a few gas-works have introduced Cooper's process; and, according to information received by the author from highly trustworthy sources in 1886, there was but little prospect of its more general adoption, as the extra yield of ammonia is counterbalanced by several drawbacks.

2nd. *By means of Hydrogen.*—R. Tervet (B. P. 1842, 1883) passes hydrogen over coal, shale, &c. in the retorts during distillation, or over the coke remaining therefrom. The hydrogen is to be obtained as in the manufacture of water-gas, or by passing coal-gas over highly-heated coke. It should be used largely in excess of the quantity theoretically sufficient to combine with the nitrogen of the coke; and the same hydrogen is several times used over again in the retorts. This process is discussed at length by Tervet himself† in a paper, from which it appears that his experiments were only made on a minute scale. He obtained ammonia equi-

* Journ. Soc. Chem. Ind. 1883, p. 438; 1884, p. 12.
† Journ. Soc. Chem. Ind. 1883, p. 445.

valent at most to 83 lb. of sulphate from one ton of coal; but when working with somewhat larger quantities (2 ounces of coal) the results fell off to 39–67 lb., and no experiment whatever seems to have been made on a working scale; nor is there any clue as to the probable cost of the process. We must therefore refer to the original for details.

3rd. *By means of Steam.*—The processes belonging to this class are hardly applicable to real illuminating-gas, and will therefore be treated separately later on.

Ammonia recovered from Coal-gas directly, without Scrubbers.

F. J. Bolton and J. A. Wanklyn (G. P. 16788) pass the crude gas, freed from tar, but not scrubbed, through a purifier in which superphosphate is spread out on trays; thus an ammoniacal manure is formed without having to collect and distil gas-liquor, and without wasting sulphuric acid. This process is extended by a further patent (B. P. 2709, 1882) to the gases from coke-ovens and blast-furnaces. These are passed through pipes into which superheated steam is injected, in order to remove the tar. In these pipes plates of wire-netting or corrugated sheet-iron are placed longitudinally, to catch tar and soot. The gases are then passed through perforated trays, containing superphosphate, gypsum, or coke moistened with sulphuric acid, to condense the ammonia; if rich in ammonia, they are first passed over shallow pans filled with sulphuric acid.

Practical experiments made with this process have been described by Bunte *. The superphosphate employed was made from Mezillones phosphates, and was first neutralized with gas-liquor to prevent any free sulphuric acid from absorbing the heavy hydrocarbons of the gas. The gas was passed over this, after coming from the scrubbers, with 60 grams of NH_3 per 100 cubic metres; after passing through the superphosphate the ammonia went down to 3·4 grams. In a second experiment, the scrubbed gas contained from 60 grams NH_3; when scrubbing was discontinued, 108 grams per 100 cubic metres: the gas issuing from the superphosphate apparatus contained at first 8 or 9, later on 12 grams; with increasing saturation of the superphosphate, at last 59 grams NH_3. If this process were to be introduced on a large scale, it would

* Dingler's Journal, vol. ccxlv. p. 40.

evidently be necessary to provide a series of purifiers, worked methodically, like oxide-of-iron purifiers, so that the gas should always pass in the end through fresh superphosphate.

Vorster and Grüneberg (G. P. 21837) pass coal-gas over trays charged with a mixture of infusorial earth (*Kieselghur*) or flue-dust and sulphuric acid, in order to retain ammonia. Another patent (G. P. 25466) claims the use of a large number of other porous materials for the same purpose.

A. P. Price (B. P. 6983, 1884) claims the use of sulphuric and sulphurous acid, and of potassium, sodium, or ammonium phosphate, for retaining the ammonia present in coal-gas.

Ammonia from spent oxide of iron

is very frequently recovered by simple lixiviation, acidifying with sulphuric acid, and evaporation. Such sulphate is often very impure, and especially very frequently contains large quantities of sulphocyanides. Th. Richters (G. P. 15206) for this purpose washes or steams the spent oxide every time before it is regenerated, preferably by treating it with air in a box fitted with divisions. In this way the regeneration is combined with the recovery of ammonia, since the process of oxidizing the ferrous sulphide to oxide and free sulphur evolves so much heat that the ammonia is driven off, and can be washed out of the escaping air by means of acid.

2. Production of Ammonia by treating Coal or Shale with Steam.

We have seen (p. 546) that only a small portion of the nitrogen of coal is converted into ammonia in the ordinary process of gas-making, and that the greater portion remains behind in the coke. A similar circumstance takes place in the distillation of bituminous shale, as carried out especially in Scotland. Hence have arisen a number of attempts at obtaining a much larger quantity of ammonia by special treatment. We may class among them already the processes enumerated in the last section; but while these still aimed at producing at the same time ordinary illuminating-gas as the principal product, we shall now speak of those processes which treat the coal for ammonia as a principal product, and obtain a gas not fit for lighting-, but only for heating-purposes, more or less like the well-known "water-gas." This arises from the fact that all these processes operate by means of *steam*. We

treat, of course, not of the operation of steam for improving producer-gas generally, but only in connection with increasing the yield of NH_3.

W. Young and G. T. Beilby (B. P. 5084, 1882) introduce coal-dross, shale, peat, &c. in a fine state of division into highly heated retorts, where it is consumed in an atmosphere of steam and air, with the production of a heating-gas rich in ammonia, along with undecomposed steam. This gas is cooled down to a certain extent, and the ammonia is then taken out by sulphuric acid, after which the gas is then ready to be used as fuel. G. Beilby has given a detailed description of that process *. Its principle is: distilling coal first in a current of steam, and burning the coke, which retains about 60 per cent. of the nitrogen, in a mixture of steam and air, the former being in such large excess as to preserve from decomposition the ammonia derived from the nitrogen of the coke. When this process is properly carried out, ammonia is produced equal to from $\frac{3}{5}$ to $\frac{4}{5}$ of the nitrogen of the coal, or from three to four times as much ammonia as is produced by the most efficiently performed destructive distillation. This result, however, can only be obtained by the partial or total consumption of the carbonaceous residue, so that the process is only applicable to the production of gas, not of coke, from coal. One half of the fixed carbon of coal is oxidized by the oxygen of steam, setting free an equivalent amount of hydrogen. The gas obtained is very much richer in hydrogen than ordinary producer-gas, or even the gas from the Wilson producers, where steam is also used, and is therefore a more valuable fuel. This is proved by the following analyses:—

	Wilson gas.	Young and Beilby gas.
Carbon dioxide.....	7·14	15·40
Hydrogen.....	12·15	34·53
Carbon monoxide.....	19·83	10·72
Methane	3·91	4·02
Nitrogen	57·24	35·33
	100·27	100·00

This principle has been carried out by two different forms of gas-producer.

* Journ. Soc. Chem. Ind. 1884, p. 216; comp. also 1885, p. 220; and Watson Smith's Report, ibid. p. 472, which is reproduced in the following.

The first form is designed for supplying the heat to shale-retorts. It consists of a vertical retort built of brick, closed by a door at the top, and provided with an exit pipe which connects the retort with a system of mains and condensers. At its lower end the retort terminates in a closed fireplace as ashpit, with regulating doors or dampers. The dross or small coal is introduced by the top door, and, resting on the firebars, fills the retort from top to bottom. The upper part of the retort, being surrounded by flues through which fire-gases are led, is kept at a full red-heat. The coal at this part of the retort is distilled, and parts with gases and vapours, which pass away by the exit-pipe to be cooled and condensed. As the coke passes down in the retort it is met by a current of steam, which is partly decomposed, burning the carbon, and producing ammonia and "water-gas," which pass off along with the other volatile products. When such a coke as has escaped the action of the steam reaches the firebars, it is turned into carbonic oxide by a regulated admission of air. This red-hot carbonic oxide passes off by ports at the lower end of the retort, and is burned in the flues surrounding the shale-retorts. The gases from the upper part of the retort, after having been deprived of their condensable constituents, are also returned and used in firing the retorts. By this system of firing, less fuel is used than by the open furnace, and the ammonia and tar recovered from the coal more than pay its first cost. About 200 of these retort-producers are in use in Scotch oil-works.

The second form is for the production of gas for firing steam-boilers or for metallurgical operations. The shell of the retort is built of grooved bricks as before, but it is of circular section, and of much larger diameter than the early retorts. The top is closed by a shallow hopper of cast iron, with two small charging-doors; through the centre of this hopper a large iron pipe is led halfway down the retort. This pipe is for the exit of the gases, and passes up into a large dust-box which runs along the bench. From the dust-box the gas is conveyed by large pipes to the condensers and exhauster. The bottom of the brick retorts rests on an iron snout-piece, which is provided with a door at the outside of the setting. The steam and air are blown in at the front of this snout-piece. The gas and air for heating the setting are led up by pipes between the walls of the building, and are thereby heated before they take fire. The fire-gases surrounding the retorts are

drawn downwards by chimney draughts, and before entering the main flues at the bottom of the setting they give up their heat to the iron snout-pieces, through which the steam and air are entering.

Gas-Condensers and Scrubbers.—In carrying out the process of gasifying carbonaceous residues in excess of steam, a great deal of heat is carried away from the operation by the large quantity of gas produced. To recover a part of this heat, and to make it again available in the process, certain forms of regenerative condenser have been devised. In these the hot gases from the retorts pass through tubes which are immersed in water or are kept wet by a shower or spray of water. The tubes are enclosed in a box or case through which a current of air is forced. The air becomes saturated with water-vapour to an extent depending on its own temperature and that of the wetted tube-surface. This saturated air, by the further addition of steam, is available for the incineration of the coal in retort gas-producers. As the principal outlay of heat in the vaporization of water is that portion which is latent in the steam, the economy of this method of producing water-vapour from heat of comparatively low grade is very evident. Air at 65° C. takes up one fourth of its weight of water, at 74° one third, at 80° one half, at 85° an equal weight, and at 93° twice its weight; it is therefore possible to raise into vapour large quantities of water by means of a comparatively small volume of air. Condensers of this construction have been working satisfactorily in the Clippens Company's Works at Pentland for nearly two years (1885).

Beilby states that of 100 parts of the nitrogen contained in bituminous shales (amounting to about 1 per cent.) there is recovered in distilling them in the usual manner for the production of paraffin oils: 17·0 as ammonia in the watery distillate, 20·4 as alkaloidal tar, 62·6 in the residual coke. When the distillation was carried on, first at a low red-heat, and the residue was afterwards subjected to a bright red-heat in the presence of steam, only 4·9 per cent. of the total nitrogen was left in the coke, 74·3 per cent being recovered as ammonia, and 20·8 as alkaloidal tar. A certain proportion of air may be mixed with the steam without seriously reducing the yield of ammonia. This has the advantage that a certain amount of heat is generated within the retort, and less heat has to be supplied from the outside.

Ingenious as the system of Young and Beilby is, we can hardly expect it to make much way at the present prices of ammonia. It must also be considered that the conditions for producing a maximum of ammonia, and those for turning out the best possible water-gas, are opposed to each other. For the former, the temperature ought to be kept down, if possible, below 500°, since ammonia, under favourable circumstances, begins to be decomposed rather below 500°, and is fully split up at 780°. But in order to realize as nearly as possible the theoretical reaction of forming water-gas,

$$C + H_2O = CO + H_2,$$

the temperature ought to be at least 900° C.; below this the reaction

$$C + 2H_2O = CO_2 + H_4$$

gets the upper hand. In fact the best temperature for the formation of good water-gas is about 1000°.

This difficulty can be overcome only by employing an excess of steam. H. Grouven, in his analytical process for estimating the percentage of nitrogen in organic substances, passes through the apparatus a quantity of steam equal to 20 or 30 times the weight of the substance. W. Foster (see below) used 16 times the theoretical quantity. This is evidently impossible to apply on an industrial scale; but Young and Beilby have found that by mixing steam and air, 60 or 70 per cent. of the nitrogen can be obtained on the large scale as ammonia, with an expenditure of only $1\frac{1}{4}$ parts of steam to 1 part of coal. That, however, the heating-gas obtained by their mode of operation is of a somewhat poor description, can be seen from the analyses quoted above.

It must not be forgotten (and Beilby, in the above-quoted communication, fully acknowledges this fact) that, as early as 1878, Grouven (compare p. 540) had recognized that the introduction of superheated steam in carbonizing organic substances greatly increases the quantity of ammonia obtainable therefrom. Long after him, and also some time after Young and Beilby (whose patents date from 1881 and 1882), W. Foster * drew attention to the same fact. By using an enormous excess of steam (16 times the theoretical quantity) he was able to convert 61·6 per cent. of the nitrogen of coke into ammonia, 35 per cent. remaining behind,

* Proc. Inst. Civil Engineers, 1883–1884, vol. lxxvii. part iii.

and 3·4 per cent. being unaccounted for. He assumes (but without any data to warrant this assumption) that on the large scale the amount of steam required would be "not unduly in excess of the theory." His calculations concerning the thermal value of water-gas are quite incorrect *.

L. Mond (B. P. 3923, 1883) likewise utilizes the fact that a low temperature and the presence of steam in gas-producers are conducive to the formation of ammonia. Hence he introduces into the furnace a limited supply of air, loaded with water-spray or steam in large quantity. The resulting gases are said to be richer in hydrogen, and to have a higher heating-power, and the tarry matter to be richer and larger in quantity. The temperature may also be kept low by the use of air partly deprived of oxygen, *e. g.*, furnace-gases. The ammonia and tar are collected by cooling and condensing; or the ammonia may be absorbed without cooling by a solution of calcium chloride or magnesium chloride, or by sulphuric acid. The point of novelty claimed is, charging the limited supply of air with so large an excess of steam or water that the temperature of combustion does not exceed a dull red heat. [Probably the production of ammonia is very much increased in this way, as proved by the preceding inventors; but in the absence of other information it is doubtful whether the heating-gas obtained is of good quality.]

In a further patent (B. P. 8973, 1885) Mond describes special means for cooling and condensing producer-gas. He passes it through a scrubber, in which it is cooled to 40° by a current of water. This water, loaded with ammonia and tarry products, is afterwards cooled by another stream of water flowing in the opposite direction; it is then again passed through the scrubber and again cooled, and so on, the same water being constantly used. The steam in the producer-gas being condensed by this treatment, a quantity of water equal to the condensed steam is drawn off at intervals, and from it the ammonia is recovered. To obtain the latter in the form of sulphate at once, the producer-gas is scrubbed with very dilute (2-per-cent.) sulphuric acid; the solution of ammonium sulphate thus obtained is used over again, fresh sulphuric acid being added after each absorption, to restore the original acidity. This operation is continued till a sufficiently

* Comp. ibid. pp. 65 and 76.

concentrated solution of ammonium sulphate is obtained to separate the salt from it. The tar is separated in the usual manner, and the residual gases are used as fuel. This method is said to effect a saving of most or all the fuel now used for raising steam for the purpose of working gas-producers under the patents Nos. 3821 and 3923, of 1883 (the former of these patents does not refer to the recovery of ammonia).

A process, very much like Young and Beilby's, has been patented by G. R. Hislop (B. P. 5252, 1882). H. Simon and Watson Smith (B. P. 4871, 1883) have patented the injection, into gas-retorts, coke-ovens, or gas-producers, of steam along with hydrocarbons in a liquid or gaseous form. Whilst the oxygen of the steam unites with the carbon, a portion of the hydrogen set free unites with the nitrogen of the partially decomposed coal, forming ammonia; a portion also of the hydrogen unites with the sulphur of the fuel, so that the quality of the coke is improved by this treatment. This process has only been carried out experimentally up to the present. A similar object is aimed at by the process of H. Kenyon (B. P. 1016, 1886).

A. French (B. P. 5945, 1885) claims the following invention :— Any material containing carbon, nitrogen, sulphur, and common salt or another suitable chloride, is heated in a kiln, air and steam being injected during the heating-process. The kiln is worked continuously. The reaction said to take place is expressed by the following equation :—

$$2NaCl + H_2SO_3 + 3H_2O + 2N + C = 2NH_4Cl + Na_2SO_4 + CO_2.$$

Nearly the whole of the nitrogen is said to be obtained as ammonium chloride, a small portion of it combining " with carbon and chloride, hydrogen, carbon monoxide, or sulphurous anhydride, to form various cyanogen compounds." I shall abstain from criticising this proposal, but refer to Solvay's and Wagner's experiments (p. 519).

3. Ammonia from Coke-ovens.

Since the recovery of ammonia as a by-product of coke-making is always carried on *pari passu* with that of tar, we have already described this industry in full detail in Chapter II., p. 38 *et seq.* We have also seen (p. 39) what proportions this industry has already assumed, what quantity of ammonia might be got from

that source, and that it is just this enormous accession to our sources of ammonia (and tar) which, even at its commencement, is keeping down the prices and making the recovery of by-products in coke-making for the present a process of doubtful economy. Still it can hardly be doubted that it is only a question of time when the enormous waste of useful matter now going on in coke-making will be a subject of the past, and when it will become wonderful that it was ever allowed to go on, after it had once been recognized that this need not be the case, and that good coke can be made along with tar and ammonia. Undoubtedly a certain depreciation of prices may have to take place; so long as a large quantity of the tar has to be burned as fuel, in which case it may claim to be of decidedly more value than retort-coke, its price can never greatly exceed that amount; and the price of ammonia will not merely be kept down by the over-production, but also by the competition of nitrate of soda. But fortunately we are not in the situation that no reasonable outlet can be found for the products in question; just as there is no limitation to burning tar as fuel, and that at the gas-works themselves, so agriculture is able to take up practically all the ammonia which industry may offer to it, if only the price is low enough. Indeed, in this seems to be the only chance of maintaining a considerably larger population out of the produce of the soil than is done at present. But of course the profits of gas companies on tar and ammonia will inevitably be greatly reduced, and compensation will have to be sought elsewhere.

Concerning the details of condensing-apparatus, we refer to Chapter II.; also to Bolton and Wanklyn's proposal for treating the gases by superheated steam, and then passing them through commercial superphosphate in order to absorb the ammonia (p. 549). We only mention here a patent of P. Frauencross and H. Strack (G. P. 32691), according to which hot coke-oven gases are passed through a mixture of coal- or coke-cinders (ashes), or they are produced in metallurgical operations, with coal-duff and lime, and thence passed into the ordinary condensers.

4. Ammonia from Blast-furnace Gases.

The general principles of the recovery of ammonia, along with a certain description of tar, from blast-furnace gases have been

mentioned in Chapter II., p. 85; and we must, in the first instance, refer to that description, more especially of the Gartsherrie process (Alexander and M'Cosh's). In this place we only mention those methods which, neglecting the tar, exclusively aim at recovering ammonia from blast-furnace gases.

Swindells and Lancaster (Fr. P. 115832, of 1876) believe they can recover, not merely the preformed ammonia, but also that obtainable by the decomposition of cyanogen compounds contained in blast-furnace gases, by means of superheated steam. The gases, after mixing with this, are passed through red-hot fuel, then through milk of lime, and finally through red-hot chambers filled with broken bricks, whereupon they are scrubbed for NH_3.

Gavin Chapman (B. P. 5523, 1881) passes the furnace-gases through a chamber in which there is arranged a set of perforated disks. The perforations, through which the gases are made to pass, are alternate, so that the perforation of one disk corresponds to a solid part of the next. The disks are fixed on a horizontal rotating shaft, and their lower parts dip in a vessel containing acid. The lid covering the disks also dips into the liquid, whose evaporating water must be replaced from time to time. Another patent of the same inventor's (B. P. 6406, 1884) contains some modifications of this process.

G. Neilson (B. P. 440, 1882) places a very large number of plates, made of earthenware or otherwise, so as not to be acted upon by acids, with interstices between them, in a chamber, and keeps them sprinkled with a dilute acid, while the gases are passed up between the plates; the ammonia salts formed drain off at the bottom.

John and James Addie (B. P. 4758, 1882) fix the ammonia in the gases by mixing therewith sulphurous, or sulphuric, or hydrochloric acid in the form of gas or vapour, and subsequently condense and recover the ammoniacal salts formed. Their process has been discussed by A. Wilson*. It was in the first instance devised in order to avoid the necessity of cooling the enormous amount of gases evolved from a blast-furnace, being thirteen times as much as that coming from a gas-retort for the same quantity of coal. The process has been successfully carried out at the Coat-

* Journ. Soc. Chem. Ind. 1883, p. 458.

bridge works, and produces sulphate of ammonia of the finest quality. The method is based upon the treatment of the furnace-gases with sulphurous-acid gas, which is allowed to mix with them at any convenient part of the flue along which they pass. The result is the instantaneous formation of sulphite of ammonia, which is carried along by the current of gases. These are then washed in a perpendicular scrubber, the water being kept in circulation by a pump. When this system is applied to the treatment of producer-gas, whose temperature is much higher than that of blast-furnace gases, the scrubbers must be cooled from the outside by a shower of water. In the case of the treatment of gases not exceeding 260° C., all the water is used inside the scrubbers, and comes out as strong liquor. The specific gravity may be raised up to 40° or 50° Tw., if necessary, by the solution of salts of ammonia. This liquor is then converted into sulphate of ammonia by distillation in the ordinary way; but it may be employed for many purposes as it stands, without conversion into sulphate, such as, for instance, the production of ammonia for the ammonia-soda process, or for the manufacture of liquor ammoniæ. The sulphite of ammonia thus obtained is always more or less mixed with sulphate and hyposulphite; but this, of course, is of no consequence, as the distillation with lime brings off the whole of the ammonia. The combination of the ammonia is shown by the following analysis of the crude liquor of 15° Twaddell :—

	Per cent. weight in volume.			
Sulphate of ammonia	2·57	containing	NH_3	0·66
Sulphite of ammonia.....	3·44	„	„	1·01
Hyposulphite of ammonia...	4·18	„	„	0·96
Total ammonia salts	10·19	„	„	2·63

Another crude liquor, evaporated to dryness, gave a salt showing the following composition (Tatlock's analysis) :—

Ammonium sulphate	36·13	per cent.
„ sulphite	19·75	„
„ hyposulphite	33·10	„
Sodium sulphate	8·58	„
Free sulphuric acid *	trace.	
Insoluble	0·03	„
Organic matter	2·11	„
	100·00 †	
Total ammonia	20·31	per cent.
Equal to sulphate of ammonia	78·85	„

The sulphurous acid used in this process is obtained from sulphurous shale, coal brasses, pyrites, &c., burnt in a retort by means of a forced current of air.

With regard to the question as to whether gas treated in this manner carries away any sulphur which might prove objectionable in metallurgical or other processes for which the gas is subsequently employed, it is interesting to quote the following testing (by Dr. Clark) of Messrs. Addie's gas-flue beyond the scrubbers, the apparatus being worked with excess of sulphurous acid in the ordinary way :—

Sulphur per cubic foot of gas	0·1	gram.
„ per ton of coal burned	1·85	lb.
„ per cent. of coal burned	0·08	

Hence the sulphur in excess is only about one tenth of the amount which must exist originally in the coal itself.

Instead of sulphurous acid, R. Main and W. Galbraith (B. P. 10448, 1884) bring the gas from blast-furnaces, or that evolved in the destructive distillation of coal, shale, &c., into contact with a spray of hydrochloric acid, and afterwards convert the ammonium chloride into sulphate. Their process does not seem to be as economical as Addie's.

J. Dempster (B. P. 11250, 1884) places between the blast-furnaces and the steam-boilers or stoves where the furnace-gases

* How can free sulphuric acid exist in the presence of sulphite and hyposulphite?

† *Sic* in the original; the real sum total is 99·70.

are to be burned an ordinary ammonia-still, with its usual sulphate apparatus, "dust-boxes," and "condensers." The gases are then taken to washers and scrubbers, where the last traces of ammonia are absorbed.

Körting Brothers * have devised a special arrangement of pipes for cooling and washing the waste gas, as shown in figs. 141 and 142. The tubes are arranged in three ranks; and connections between the individual pipes of each rank are so made that the gases pass

Fig. 141.

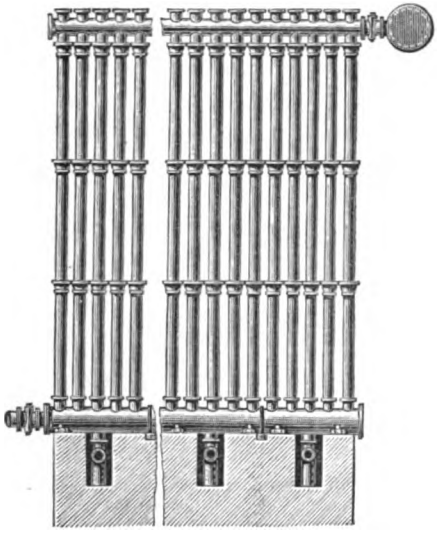
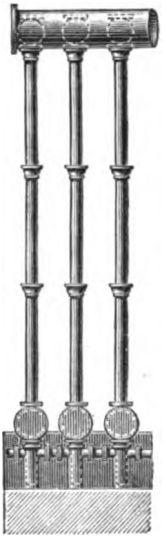


Fig. 142.



up through one set of five pipes and down through the next. A system of 450 tubes, of 1 foot diameter and 12 feet long, gives a total surface of 18,300 superficial feet cooled by the air. An injector may be advantageously applied at different points of such a system.

We shall also show here the washing-chambers, devised by Young and Beilby, intended to decrease the velocity of the stream of gas, and thus to allow a complete separation of tarry matters p. 553). In the arrangement (fig. 143) the gases are introduced by the conduit *g*, and enter the chamber by the openings *e e*,

* Dingler's Journal, ccliv. p. 260; Journ. Soc. Chem. Ind. 1885, p. 220.

covered with leaden bells. A fine spray of water, or acid, is maintained during the passage of the gas. The washed gases pass away by *g*, the washings by *u*.

Fig. 143.

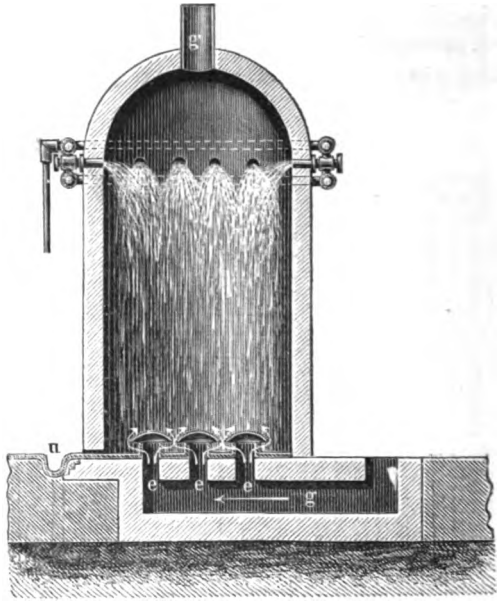


Fig. 144.

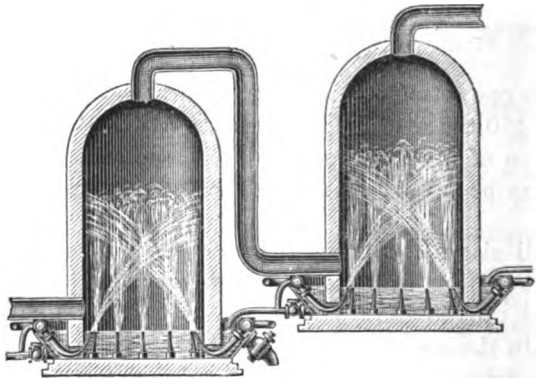


Fig. 144 shows a somewhat more advantageous arrangement, consisting of a series of chambers built on different levels, so that

the liquid employed for washing can be introduced at the opposite end of the system to that at which the gas enters, and passes simply by gravity through the whole series, until spent. Thus it is not necessary to lift the liquid to the top of the chamber and there spray it. The size of the chambers is such that for 100 cubic feet of gas passed through in 24 hours, at least 0·5 cubic feet of space is provided. Large chambers, in which the cooled gases can come to rest and deposit their particles of tar, appear to be most suitable for the complete separation of the tar.

5. Ammonia from Producer-gas.

We have had occasion before to mention the recovery of ammonia from the gaseous fluid made in gas-producers or "generators"; thus in connection with the processes of Mond and of Addie (p. 558), which Wilson believes to be applicable to his gas-producers. Evidently most of the processes described in the preceding and in the following sections would apply to gas-generators, provided the ammonia produced paid for the cost of the operation, and that the latter did not injure too much the efficiency of the gaseous fuel, which in any case it will do by cooling it.

We may also mention the process of Fogarty (p. 527), although in this the ammonia originally present in producer-gas plays only an insignificant part.

6. Ammonia from ordinary Products of Combustion.

We comprise in this section the attempts at recovering ammonia from other sources than those previously enumerated; especially from the products of combustion in ordinary cases, or where they are mixed with vapours more charged with ammonia, *e. g.* when carbonizing bones in pot-furnaces. In these cases the methods hitherto enumerated are not sufficient to sift out, as it were, the very small quantity of ammonia from among an enormous volume of diluent gases; nor can it be said that this problem has been satisfactorily solved by any inventor.

Fr. Lorenz (B. P. 6008, 1882) employs the gases from bone-char furnaces first to raise steam, and then passes them through regenerators, to give up most of their heat. After this they are mixed with hot steam; the mixture of gases and steam is sent into a scrubber; the cold gases coming from the scrubber are first re-heated, in order to again saturate them with steam, by being made

to traverse the regenerators in a direction opposite to that of the gases coming direct from the furnaces, and are then sent into another scrubber fed with dilute sulphuric acid. [The idea of mixing the furnace-gases, containing an exceedingly minute quantity of ammonia, with steam, or water in a fine spray, vaporized by the heat of the gases, in order to make the ammonia more easily condensable in a scrubber, because only in this way would there be a sufficient contact with water for all the dispersed molecules of ammonia, was suggested to the "inventor" in a detailed memoir sent to him by myself on June 29, 1881. This idea has been incorporated in the above patent, without leave being given, or any notice being received, by me.] The German patents Nos. 26638 and 26979 (of 1882) describe the same "invention."

H. Neumeyer (G. P. 24511) employs hot sulphuric acid for absorbing ammonia from gaseous mixtures. The acid is converted into a fine spray, by issuing under pressure from holes in a vertical pipe, made of an alloy of lead and antimony, and strikes against the sides of an outer pipe, while the gases containing ammonia travel through the annular space between the pipes. The liquor collecting at the bottom is heated by a steam-coil, and by a force-pump is pumped back into the spray-producer. Thus a hot and concentrated solution is obtained, from which ammonium sulphate separates on cooling.

H. Wellstein (G. P. 28762) likewise employs a spray of heated sulphuric acid, which strikes against the cover of the chamber through which the gases containing ammonia are made to travel; whenever a certain quantity of liquor has collected at the bottom of the chamber, it passes through an automatically opening valve into a pulsometer, where it is subjected to heating from without, and the vapour generated thereby causes the pulsometer to act, and to force the acid liquor back again into the upper reservoir, till it is completely saturated with ammonia.

The Société anonyme Lorraine industrielle de Hussigny (B. P. 5828, 1884) recommends the absorption of ammonia from furnace-gases by calcium chloride. The mixture of calcium carbonate and ammonium chloride formed is either to be used as an ammoniacal manure, or, by heating, sesquicarbonate of ammonia can be obtained, which is to be employed in the ammonia-soda process.

CHAPTER XIII.

THE COMPOSITION AND ANALYSIS OF AMMONIACAL LIQUOR, AND PROPERTIES OF ITS CONSTITUENTS.

We have seen in the last Chapter that, by subjecting gases containing ammonia to a combination of cooling and washing processes, we obtain an aqueous solution of ammonium salts which we call "ammoniacal liquor." We do not in this place include in our consideration those liquors obtained by the direct action of sulphuric, sulphurous, or hydrochloric acid on such gases, but only those obtained by the action of water alone. By far the most important source of ammoniacal liquor is the purifying process to which ordinary coal-gas must be submitted, and hence such liquor is commonly called "gas-liquor." The solutions obtained from coke-oven or blast-furnace gases are equally derived from coal, and are altogether similar in character to gas-liquor, and they are treated in exactly the same way, so that we shall in the future always include them in our consideration along with the former. This would also be the case with liquors obtained from gas-producers, if that became a working process. Even the liquors obtained from fermented urine, or by the destructive distillation of bones and other animal refuse (pp. 528 and 532), although not identical in composition with those derived from the treatment of coal, are so similar to them that the same principles are followed in working them up into commercial articles.

Composition of Ammoniacal Liquor.

Ordinary gas-liquor contains the following substances :—

a. *Volatile at ordinary temperatures.*

Ammonium carbonates (mono-, sesqui-, bi-).
Ammonium sulphide, $(NH_4)_2S$.
Ammonium hydrosulphide, $NH_4.HS$.
Ammonium cyanide.
Ammonium acetate (?).
Free ammonia*.

b. *Fixed at ordinary temperatures.*

Ammonium sulphate.
Ammonium sulphite.
Ammonium thiosulphate (hyposulphite).
Ammonium thiocarbonate.
Ammonium chloride.
Ammonium sulphocyanide (thiocyanate).
Ammonium ferrocyanide.

Also the salts of organic bases, especially those of the pyridine series; phenols, and other matters of a tarry or "empyreumatic" character.

The more important of these substances will be described towards the end of this Chapter. The term "fixed" in this case is not to be understood in its absolute sense, but in this sense, that the compounds of ammonia with carbonic and sulphhydric acids can be removed from their solutions by simply exposing them to a sufficiently prolonged boiling, certainly not in the state of unchanged vapours of ammonium salts, but dissociated into less complicated compounds; but the ammoniacal salts, called "fixed," are not removed from their solutions by boiling, or are only very partially decomposed by very prolonged heating of the solutions, so that the ammonia contained in them must be recovered by heating the solutions in the presence of lime, which sets the ammonia free. This is an important distinction in the practical working-up of gas-liquor.

The proportion of the total ammonia to the "fixed" ammonia varies according to circumstances. Fixed ammonia naturally

* The presence of free ammonia in gas-liquor is doubted by most chemists, but is asserted by two competent observers, Gerlach and Tieftrunck (Wagner's Jahresb. 1877, p. 1065).

occurs in much larger proportion in the hydraulic main, where the first condensation takes place, than in the condensers and scrubbers; it may amount to more than 50 per cent. of the total ammonia in the former, against 1 or 2 per cent. in the latter. This proportion is moreover influenced by the composition of the coal. Thus the percentage of ammonium chloride in the gas-liquor will naturally depend upon the percentage of chlorine in the coal distilled. The percentage of fixed ammonia will also be influenced by the temperature of the gas-retorts, by the temperature to which the gas-liquor has been exposed, by its exposure to the air (which oxidizes sulphide into thiosulphate and perhaps higher than that), and by the general method of washing and scrubbing the gas (J. H. Cox, Journal of Gas-Lighting, &c., Report of the Leeds Meeting, Oct. 6, 1883).

The following Tables (pp. 568, 569) are constructed from the materials supplied in the just-mentioned paper by Mr. Cox; but the thiosulphate is not, as there, included in the "volatile" salts, since experiments made by myself have convinced me that it hardly decomposes on boiling more than the chloride.

According to Wanklyn (Gas-Engineer's Chemical Manual) virgin gas-liquor from the first parts of the plant may contain free ammonia, because this is more quickly absorbed than the other constituents, but in passing through the scrubbers enough CO_2 is absorbed to convert all the free ammonia into carbonate. If the same liquor is used over and over again for scrubbing, a good deal of the ammonium sulphide is also converted into carbonate, H_2S being given off.

Detailed analyses of gas-liquor, obtained under different conditions, are given by L. T. Wright*.

According to information received from one of the largest German ammonia-works, it is calculated there that liquor from English coals contains from 15 to 20 per cent. of the total ammonia in the "fixed" state, that from Westphalian coals 5 to 10 per cent.; while in liquor from Saxon coal the fixed ammonia may amount to two or three times as much as the volatile.

* Abstracted from the 'Journal of Gas-Lighting,' in the Journ. Soc. Chem Ind. 1886, p. 655.

I. Table showing the Properties and Composition of eight samples of Gas-liquor, obtained from the same Coal, but taken from different points in the Condensing- and Scrubbing-plant.

	Condensed in the hydraulic main.	Another point of the hydraulic main.	Liquor from first condenser column.	From second condenser column.	From third condenser column.	From fourth condenser column.	From first washer.	From finishing washer.
Colour	Very dull orange, turned black in air.	Ditto.	Colourless.	Almost colourless.	Brown-red, from light tar-oils.	Dark brown, from tar-oils	Colourless.	Colourless.
Specific gravity in deg. Twaddell at 15°·5 C.	2¼	2½	7	15	23	24	4½	2
Ounces by distillation test	6·1	6·0	16·2	36·1	53·0	58·0	16·5	8·3
Ounces by saturation test	2·7	2·8	15·9	35·7	52·5	57·4	16·1	8·1
Am. sulphide, grams per gallon	364	440	2430	5000	7905 NH_3	8440	1592	1220
$=NH_3$ „ „	182	220	1215	2500		4220	796	610
Am. carbonate, „ „	564	510	3384	8120		12126	4512	1690
$=NH_3$ „ „	200	81	1200	2880		4300	1600	600
Am. thiosulphate, „ „	122	82	Trace	125	352	765	230	135
$=NH_3$ „ „	28	19	Trace	41	81	176	51	31
Am. sulphate, „ „	8	34	.....	.....	.....	.....	.....	.....
$=NH_3$ „ „	2	9	.....	.....	.....	.....	.....	.....
Am. sulphocyanide, „ „	112	130	91	Trace	.....	.....	112	27
$=NH_3$ „ „	25	29	2	Trace	.....	.....	25	6
Am. chloride, „ „	1552	1455	119	155	201	107	88	38
$=NH_3$ „ „	493	462	38	50	64	34	28	12
Am. ferrocyanide, „ „	.....	Trace	22	41	125	375	.....	.....
$=NH_3$ „ „	.....	.....	5	10	30	90	.....	.....
Total ammonia, grams per gallon	930	920	2460	5480	8080	8820	2500	1260
Percentage of fixed ammonia in the total ammonia.....	59 p. c.	56 p. c.	1·8 p.c.	1·85 p. c.	2·2 p. c.	3·4 p. c.	4·2 p.c.	4·0 p. c.
Ammonia expressed as cwt. of sulphate per 1000 gallons.....	4·5	4·5	11·9	26·6	39·3	42·8	11·8	6·1
Value of liquor for sulphate-making.	Very small.	Very small.	Very good.	Very good.	Excellent.	Excellent.	Very good.	Not quite strong enough.

II. Table showing the Properties and Composition of various samples of Liquor from different Coals and from different points in the Condensing- and Scrubbing-plant.

	Condensed liquor, passed through scrubber.	Another sample taken at different time.	Same liquor exposed to air, high temperature.	Hydraulic main liquor.	Part condensed liquor, part hydraulic main.	From "Standard" washer before purifiers.
Colour	Yellow.	Yellow.	Bright orange.	Dull yellow.	Yellow.	Colourless.
Spec. grav. = deg. Tw. at 15°·5 .	4·5	4	3·5	2	3	4·5
Ounces by distillation test	10·00	8·25	6·90	5·60	6·60	10·00
Ounces by saturation test	8·30	7·00	4·25	3·40	4·90	10·00
Am. sulphide, grams per gallon.	960	1216	630	576	220	1180
$=NH_3$ " "	480	608	315	288	110	590
Am. carbonate, " "	2030	1156	800	.....	1692	2540
$=NH_3$ " "	720	410	283·5	193	600	900
Am. thiosulphate, " "	195	182	236	.....	174	Trace
$=NH_3$ " "	45	42	52·5	35	40	.....
Am. sulphate, " "	.....	Trace.	39	.....	9	.....
$=NH_3$ " "	.....	.....	10·5	6	2·5	.....
Am. sulphocyanide, " "	338	243	472	.....	90	.....
$=NH_3$ " "	75	54	105	36	20	.....
Am. chloride. " "	567	403	891	.....	693	32
$=NH_3$ " "	180	128	283·5	301	220	10·1
Am. ferrocyanide, " "	Trace.	.....	.....	.....	31	.....
$=NH_3$ " "	.....	.....	.....	.....	7·5	.....
Total ammonia	1500	1250	1050	860	1000	1500
Percentage of fixed ammonia ...	20	18·3	43	44	29	0·7
Ammonia expressed as cwt. sulphate per 1000 gallons	7·25	6·00	5·00	4·10	4·85	7·30
Value of liquor for sulphate-making.	Not good.	Poor.	Very poor.	Not worth working.	.....	Very good.

I. Table showing the Properties and Composition of eight samples of Gas-liquor, obtained from the same Coal, but taken from different points in the Condensing- and Scrubbing-plant.

	Condensed in the hydraulic main.	Another point of the hydraulic main.	Liquor from first condenser column.	From second condenser column.	From third condenser column.	From fourth condenser column.	From first washer.	From finishing washer.
Colour	Very dull orange, turned black in air.	Ditto.	Colourless.	Almost colourless.	Brown-red, from light tar-oils.	Dark brown, from tar-oils	Colourless.	Colourless.
Specific gravity in deg. Twaddell at 15°·5 C.	2½	2½	7	15	23	24	4½	2
Ounces by distillation test	6·1	6·0	16·2	36·1	53·0	58·0	16·5	8·3
Ounces by saturation test	2·7	2·8	15·9	35·7	52·5	57·4	16·1	8·1
Am. sulphide, grams per gallon	364	440	2430	5000		8440	1592	1220
$=NH_3$ „ „	182	220	1215	2500	7905	4220	796	610
Am. carbonate, „ „	564	510	3384	8120	NH_3	12126	4512	1690
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Am. thiosulphate, „ „	122	82	Trace	125	352	765	230	135
$=NH_3$ „ „	28	19	Trace	41	81	176	51	31
Am. sulphate, „ „	8	34	.....	.....	.....	.....	.....	.....
$=NH_3$ „ „	2	9	.....	.....	.....	.....	.....	.....
Am. sulphocyanide, „ „	112	130	91	Trace	.....	.....	112	27
$=NH_3$ „ „	25	29	2	Trace	.....	.....	25	6
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$=NH_3$ „ „	493	462	38	50	64	34	28	12
Am. ferrocyanide, „ „	.....	Trace	22	41	125	375	.....	.....
$=NH_3$ „ „	.....	.....	5	10	30	90	.....	.....
Total ammonia, grams per gallon	930	920	2460	5480	8080	8820	2500	1260
Percentage of fixed ammonia in the total ammonia.....	59 p. c.	56 p. c.	1·8 p.c.	1·85 p. c.	2·2 p. c.	3·4 p. c.	4·2 p.c.	4·0 p. c.
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II. Table showing the Properties and Composition of various samples of Liquor from different Coals and from different points in the Condensing- and Scrubbing-plant.

	Condensed liquor, passed through scrubber.	Another sample taken at different time.	Same liquor exposed to air, high temperature.	Hydraulic main liquor.	Part condensed liquor, part hydraulic main.	From "Standard" washer before purifiers.
Colour	Yellow.	Yellow.	Bright orange.	Dull yellow.	Yellow.	Colourless.
Spec. grav. = deg. Tw. at 15°·5	4·5	4	3·5	2	3	4·5
Ounces by distillation test	10·00	8·25	6·90	5·60	6·60	10·00
Ounces by saturation test	8·30	7·00	4·25	3·40	4·90	10·00
Am. sulphide, grams per gallon.	960	1216	630	576	220	1180
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Am. thiosulphate, " "	195	182	236	.....	174	Trace
$=NH_3$ " "	45	42	52·5	35	40	.....
Am. sulphate, " "	.....	Trace.	39	.....	9	.....
$=NH_3$ " "	.....	.....	10·5	6	2·5	.....
Am. sulphocyanide, " "	338	243	472	.....	90	.....
$=NH_3$ " "	75	54	105	36	20	.....
Am. chloride. " "	567	403	891	.....	693	32
$=NH_3$ " "	180	128	283·5	301	220	10·1
Am. ferrocyanide, " "	Trace.	.....	.....	.....	31	.....
$=NH_3$ " "	.....	.....	.....	.....	7·5	.....
Total ammonia	1500	1250	1050	860	1000	1500
Percentage of fixed ammonia	20	18·3	43	44	29	0·7
Ammonia expressed as cwt. sulphate per 1000 gallons	7·25	6·00	5·00	4·10	4·85	7·30
Value of liquor for sulphate-making.	Not good.	Poor.	Very poor.	Not worth working.	.....	Very good.

The following Table (by Gerlach) of the composition of some gas-liquors possesses merely a comparative value, as, for instance, ammonium sulphocyanide is not mentioned at all.

1 litre of gas-liquor contains (in grams) :—

	Chemnitz gas-works. Zwickau coal.	Saxon town. Zwickau coal.	Bonn gas-works. Ruhr coal	Treves gas-works. Saar coal.	Zurich. Saar coal.
Total ammonia.....	12·090	9·40	18·12	15·23	3·47
Ammonium thiosulphate.....	1·036	1·628	5·032	2·072	0·296
„ sulphide	0·340	0·646	6·222	2·468	1·428
„ bicarbonate	1·050	1·470	2·450	33·763	5·856
„ monocarbonate .	4·560	7·680	33·120		
„ sulphate	0·462	0·858	1·320	4·922	1·926
„ chloride	30·495	17·120	3·745		
„ salts, total	37·943	29·402	51·889	43·225	9·506

This shows very great differences, both in the total ammonia and in its distribution among the several salts, between the various liquors.

The next Table, by Gerlach, comprises the results of his own and other tests for total ammonia in sundry gas-liquors.

Coal distilled.	Grams NH_3 per 100 c. c.	Degrees Baumé.	Gas-works.
German Coals.			
Zwickau coal.....	1·209	1·6	Chemnitz.
„ and Bohemian lignite	0·908	1·66	Leipzig.
Zwickau and Burgk coal ...	0·944	1·5	Dresden.
Burgk coal.....	1·862	2·8	Freiberg.
Ruhr coal	1·812	2·1	Bonn.
„ „	1·292	1·75	Eupen.
„ „	1·826	2·25	Cologne.
„ „	1·278	1·5	Dortmund.
Saar coal	1·574	...	Augsberg.
„ „	1·523	2·5	Treves.
„ „	1·870	3·2	Zurich.
„ „	1·435	3	Munich.
Silesian coal	2·339	3	Berlin.
„ „	1·290	...	Pest.
„ and Bohemian lignite	1·030	2	Prague.

Coal distilled.	Grams NH_3 per 100 c. c.	Degrees Baumé.	Gas-works.
English Coals.			
Cannel coal; boghead	2·881	3·75	Hamburg.
English coal	3·514	4	Stettin.
„ „	2·659	3	St. Petersburg.
„ „	2·244	3·3	Trieste.
„ „	2·142	3·5	Stralsund.
Leverson Wallsend ; Old Pelton Main	2·366	4	Altona.
English coal	2·407	4	Copenhagen.
New Pelton; Ravensworth	1·785	2·75	Riga.
Old Pelton Main	1·717	3	Königsberg.
English coal	2·066	3	Stettin.
Old Pelton Main; Leverson Wallsend.....	1·345	3	Dantzic.

Valuation of Ammoniacal Liquor.

This is frequently done at the gas- and tar-works by means of the hydrometer, for the sake of convenience. But this process is most deceptive; for the ammonium salts raise the density of the solution in an unequal degree, and free ammonia (which, however, does not frequently occur) lowers it. The following Table, by Seidel *, proves how unequal are the percentages of ammonia in different gas-liquors of the same specific gravity (at 15°) :—

Degrees Baumé...	2°.	2°·5.	3°.	3°·5.	4°.	4° 5.	5°.	6°.
Specific gravity...	1·0138	1·0163	1·0208	1·0249	1·0280	1·0316	1·0352	1·0426
Per cent. NH_3 ...	1·16	1·30						
	1·42	1·43						
	1·50	1 63	1·63					
	1·77	1·77	1·76					
		1·98	1·90	1·87				
		2·18	2 10	2 00				
		2·65	2 38	2·24				
			2·45	2·40	2·55			
				2·72	2·72	2·79		
					2·90	2·85		
					3·40	3·05		
						3 40		
						3·53	3·67	3·74

Similar observations have been made by T. H. Davis †, and the

* Hofmann's Bericht über die Wiener Austellung, i. p. 194.

† Chem. News, xxxviii. p. 193.

tables on pp. 568 and 569, by Mr. Cox, completely bear out the same conclusion.

It is consequently decidedly preferable to value gas-liquor by a chemical test. Usually only the volatile ammonium salts are estimated, the ammonia of which is given off on distillation without lime, and is indicated by titrating with sulphuric acid without heating. The ammonium salts with stronger acids, *i. e.* the sulphate, chloride, and sulphocyanide, can be all the more left out of account as the ammonia thus present hardly ever amounts to more than 0·3 per cent.

The most rational way (which is also the usual one in Germany) is, to employ the ordinary standard acid, which contains 0·049 gram SO_4H_2 per cubic centimetre, and indicates 0·017 gram NH_3. When litmus is employed, a certain volume of gas-liquor, say 20 c. c., should be first supersaturated with standard acid (for which purpose 40 c. c. will suffice in most cases), and boiled to expel all carbon dioxide and hydrogen sulphide; and then the litmus solution is added and the excess of acid retitrated by standard alkali (soda or seminormal ammonia). In direct titration with acid a solution of litmus cannot be very well employed, because it is discoloured by sulphuretted hydrogen; in this case litmus paper can be employed, which, after a little practice, does not take much time; or else some of the azo-colours are employed, which permit exact working in the cold and are not affected either by CO_2 or H_2S, of which the best known is the "methyl-orange," also called "helianthine." It is the dimethylaniline-azo-benzene-sulphonate of soda, and is not to be confounded with the "tropæolines," which yield much less sharp results *.

In England it is usual to state the percentage of gas-liquor in "ounces." This refers to the number of ounces of real sulphuric acid (H_2SO_4) required for saturation by each gallon of gas-liquor, and the test is made as follows:—A standard liquid is prepared by diluting 16⅓ ounces of best rectified oil of vitriol, supposed to be equal to 16 ounces of real sulphuric monohydrate, H_2SO_4, with water to the volume of a gallon. The specific gravity of the dilute acid ought to be = 1·068, according to the usual statement. This is, however, useless without, at the same time, stating the temperature. At 15° C., an acid containing in 100 parts by volume 10

* Compare the author's observations and special directions, Chem. News, xliv. p. 288.

parts by weight of real H_2SO_4 will have the specific gravity 1·064; but it is, of course, much better not to rely upon a specific-gravity test, but to test your standard acid in the usual way, say, with pure sodium carbonate *.

The test itself is performed by measuring off 16 liquid ounces of the gas-liquor to be examined, and running in the test acid from a measure or burette graduated to liquid ounces, till litmus paper indicates neutrality. The number of the measures of acid indicates the number of ounces of real sulphuric acid required for each gallon of gas-liquor. It is generally supposed that each degree Twaddell corresponds as nearly as possible to two ounces of sulphuric acid; *e. g.* gas-liqour of 4° Tw. will saturate 8 ounces of acid. This is, however, anything but correct, as is best shown by Cox's table, pp. 568 and 569. It is therefore altogether misleading and objectionable to double the figure found by Twaddell's hydrometer, and call this the "ounces" per gallon. This is in most cases to the advantage of the buyer, for nearly in all cases the Twaddell degrees × 2 read far below the actual value of the liquor in ounces.

The test as just described is called the "*saturation test*;" it indicates none but the "volatile" ammonia. If the test-acid is correctly made to contain 100 grams of H_2SO_4 per litre, each ounce used in the test is equal to 0·3469 ounce of NH_3 per gallon, or 0·217 part NH_3 by weight per 100 parts liquor by volume.

If the *total ammonia*, including that combined with strong acids, has to be estimated, the gas-liquor is *distilled* with alkali, lime, magnesia, or baryta, and the vapours are received either into water or, better, at once into standard sulphuric acid, the unsaturated acid being afterwards determined by standard alkali (compare conclusion of this chapter). Some prefer lime, baryta, or magnesia to the alkalis, on the (unfounded) assumption that the former are better, not splitting up organic alkaloids, while equally producing ammonia.

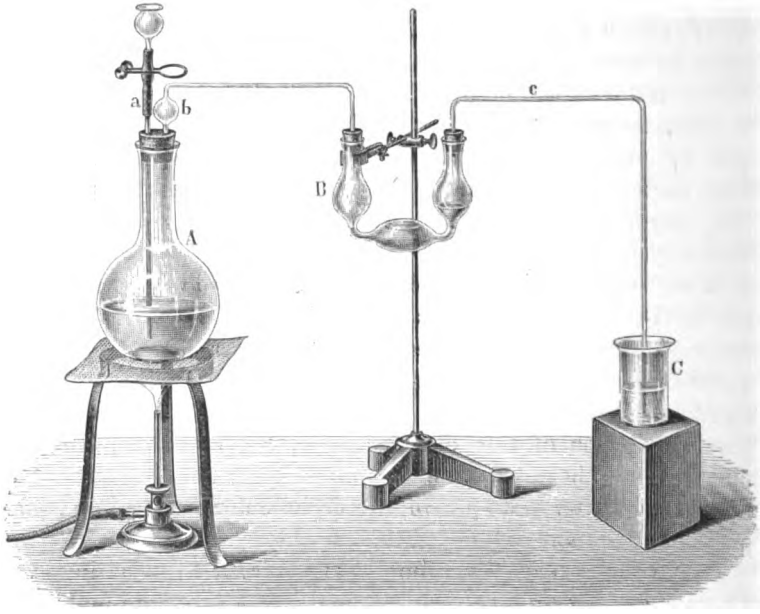
I have shown † that lime, magnesia, or soda in excess liberate equally well all the ammonia from ammonium chloride

* This operation is described in every textbook of Analytical Chemistry; also in full detail in Lunge and Hurter's 'Alkali Makers' Pocket-book' (London, 1884), p. 150.

† Journ. Soc. Chem. Ind. 1883, p. 514.

(and hence, presumably, all the "fixed" ammonia); but the distillation ought not to last less than three hours, otherwise the ammonia is not totally expelled. Hence, in analyzing pure ammonium salts it is indifferent which of the three fixed bases is employed, and caustic soda, being the simplest and cleanest to employ, is preferable to the others. The compound ammonias and other organic bases behave exactly like ammonia; they are liberated under the circumstances by either soda, lime, or magnesia, and there is no advantage to be derived from employing the latter. Lime or soda, on distilling them for three hours with an excess of ammonium chloride, liberate their full equivalent of NH_3; but magnesia, on distilling for 3 to 5 hours, only about 85 per cent. of the theoretical quantity of NH_3, possibly owing to the formation of a basic magnesium chloride difficult to decompose. Hence magnesia must always be employed in excess. For

Fig. 145.



practical purposes it must be considered that the ammonia manufacturer does not treat his liquors with magnesia, but with lime, and that hence the latter indicates the yield to be expected better than the former. Berthelot and André (Bull. Soc. Chim. xlvii.

p. 835) have proved that certain ammonium salts are not at all decomposed by magnesia, even on boiling, and only partially by lime, while soda decomposes them entirely.

The distillation test is very conveniently performed in the apparatus shown in fig. 145. A is a flask, provided with a funnel-pipe closed by a pinch-cock, for running in the caustic-soda solution; *b* is the gas-delivery pipe, provided with a bulb, and cut off obliquely below, connected with the receiver B. The latter is connected with the safety-tube *c*, dipping into the beaker C, to prevent accidental loss by spurting over of standard acid.

At some works they dispense with the funnel-tube *a*, and even with the U-tube B, employing an open flask as receiver. The flask A would then hold about 400 c. c.; it is charged with 25 c. c. of gas-liquor, to which is added 50–150 c. c. water and about 50 c. c. milk of lime; the cork is quickly put on, and thus the connection made with the receiving-flask, already charged with very dilute standard acid. The liquor in A is gradually heated to boiling, which is continued by a small flame, afterwards increased; it is unnecessary to cool the receiver. The distillation is sometimes interrupted after an hour; but this does not seem quite enough, and it is better to carry it on for three hours.

In any case we would insist that the analyst convinces himself of the complete expulsion of the ammonia, by suspending, at the close of the distillation, a moistened piece of turmeric or other test-paper in the distillation vessel above the liquid. If this indicates any alkalinity whatever, the test must be repeated.

S. Dyson * proposes the following method for a complete analysis of gas-liquor, taking, however, no account of organic bases and other substances difficult to estimate.

(a) *Determination of Total Ammonia.*—25 c. c. of the liquor is boiled with magnesia, and the evolved ammonia collected in 50 c. c. standard sulphuric acid, which is afterwards titrated back with standard soda. Suppose this showed 2·045 per cent. NH_3. [Dyson prefers magnesia to lime, because in a check experiment, where he distilled the liquor with lime almost to dryness, 2·152 per cent. NH_3 was obtained, which he, no doubt rightly, attributes to the action of lime on organic substances containing nitrogen. This action of the lime can be easily avoided by employing a more dilute solution, and not boiling to dryness. When employing

* Journ. Soc. Chem. Ind. 1883, p. 229.

magnesia, it must not be forgotten that its action is much less energetic and slower than that of lime (comp. p. 574).]

(b) *Determination of Total Sulphur.*—25 c. c. of the liquor are allowed to fall, drop by drop, from a burette into water, acidulated with hydrochloric acid and containing an excess of bromine. The excess of bromine is evaporated off, the solution filtered from the precipitate formed (which seems to consist mainly of tribromophenol), and the sulphur precipitated as barium sulphate. This yields, *e. g.*, 0·3915 per cent. S.

(c) *Determination of Sulphides.*—Zinc sulphate and ammonium chloride are added to 25 c. c. liquor; the precipitate is filtered off and well washed. The filter-paper is perforated, and small portions of the precipitate are gradually washed through into water acidulated with hydrochloric acid, and containing an excess of bromine. When the whole of the precipitate has been washed through, the solution is heated to expel the excess of bromine, filtered, and barium chloride added to the filtrate. Suppose we obtain thus 0·190 per cent. S = 0·303 NH_4. HS.

(d) *Determination of Carbonates.*—An ammoniacal solution of calcium chloride is added to 25 c. c. liquor. The precipitated calcium carbonate is filtered off, dissolved in 50 c. c. standard hydrochloric acid, and the solution titrated back with standard soda. Suppose we thus obtain 1·795 per cent. CO_2 = 3·916 $(NH_4)_2CO_3$.

(e) *Determination of Chlorides.*—50 c. c. are evaporated to dryness on the water-bath. [This might lead to some sal ammoniac being volatilized!] Water is added, and the undissolved tarry matters filtered off. The filtrate is mixed with a solution of copper sulphate and ferrous sulphate in about equal proportions (in order to remove thiocyanates), and the liquid again filtered. Nitric acid and silver nitrate are added to the filtrate, and the solution is boiled. The precipitate is allowed to settle, and the supernatant liquid poured through a filter. Before finally filtering-off the silver chloride, it is digested several times with hot nitric acid, to dissolve out the silver sulphide resulting from the decomposition of the silver thiosulphate. [This might easily lead to some AgCl being dissolved!] The silver chloride is then filtered off and weighed. Suppose we obtain 0·944 Cl = 1423 NH_4Cl.

(f) *Determination of Thiocyanates.*—This is not quite easy, and

is best done in the following way :—50 c. c. of the gas-liquor are evaporated to complete dryness, and the residue is heated to 100° for three or four hours, in order to make the precipitate of thiocyanate to be obtained later on less finely divided. The residue is then digested with strong alcohol, rinsed on to a filter, and washed with alcohol. The alcoholic filtrate is evaporated to dryness, water is added, and the insoluble organic matter filtered off. A solution of ammonium thiocyanate is thus obtained tolerably free from other ammoniacal salts (especially thiosulphate) and from organic matter. This solution is precipitated by the addition of copper sulphate and sulphurous acid (which is preferable to ferrous sulphate as a reducing agent) ; it is gently warmed (not boiled !) and, after settling, the cuprous thiocyanate, CuCNS, is filtered off. It is then washed into a flask, dissolved in nitric acid, and the liquid boiled for a considerable time. The copper is then precipitated as oxide by caustic soda; the weight of CuO $\times 0{\cdot}96$ = the equivalent amount of NH_4CNS. Suppose we obtain $0{\cdot}180$ NH_4CNS. [The volumetric method of Liddle and Barnes (Journ. Soc. Chem. Ind. 1883, p. 122) was found inapplicable to gas-liquor.]

(g) *Determination of Sulphates.*—250 c. c. are evaporated to dryness. Water is added; the organic substances filtered off, and the solution boiled with HCl. A little zinc oxide is added, the liquid filtered, and the sulphates precipitated with barium chloride. Suppose we obtain 0·019 per cent. $(NH_4)_2SO_4$.

(h) *Determination of Thiosulphates.*—This cannot be done by any direct method; but it can be arrived at by subtracting from the amount of total sulphur that existing as sulphides, thiocyanates, and sulphates. In our example :—

Total sulphur.....		0·3915
Sulphur in sulphides	0·1900	
,, thiocyanates	0·0757	
,, sulphates.....	0·0046	
	———	0·2703
Sulphur in ammonium thiosulphate.....		0·1212

$= 0{\cdot}280$ per cent. $(NH_4)_2S_2O_3$.

(i) *Ferrocyanides.*—The residue obtained by evaporating 250 c. c. of the liquor to dryness is dissolved in water, the solution filtered, and ferric chloride added to the filtrate. The precipitate

of Prussian blue is filtered off, washed, and decomposed with caustic soda. The ferric hydroxide thus obtained is, after filtering and washing, dissolved in dilute sulphuric acid, reduced, and the solution titrated with centinormal potassium permanganate. The Fe × 5·07 equals the amount of $(NH_4)_4FeCy_6$. Suppose we have found 0·0415 per cent. of this compound.

The result will therefore be that one litre of the sample of gas-liquor analyzed contains in grams :—

		NH_3.
Total ammonia	20·45	
,, sulphur	3·92	
Ammonium sulphide, NH_4HS	3·03 =	1·01
,, monocarbonate, $(NH_4)_2CO_3$	39·16 =	13·87
,, chloride, NH_4Cl	14·23 =	4·52
,, thiocyanate, NH_4CNS	1·80 =	0·40
,, sulphate, $(NH_4)_2SO_4$	0·19 =	0·05
,, thiosulphate, $(NH_4)_2S_2O_3$	2·80 =	0·64
,, ferrocyanide, $(NH_4)_4FeCy_6$	0·41 =	0·10
		20·59

The ammonia in spent oxide, according to J. Carter Bell *, is often returned in extremely varying quantity by different chemists, according to the method of analysis employed. He recommends the following method, as being analogous to the manner in which the oxide can be worked up commercially. If poor in ammonia, 10 grams are heated in the water-bath till dry. This will give the moisture, and also drive off any volatile ammonia which cannot be profitably collected in practice. The oxide is then washed with boiling water till free from ammonia salts, filtered, and the washings put into a flask. Milk of lime is added, and the contents of the flask boiled, and the NH_3 driven over into sulphuric acid. The certificate is made out as ammonia equal to sulphate; for in some cases so much sulphocyanide (thiocyanate) is present as to unfit the salt for manure-making. Bell supposes (but wrongly) that the sulphocyanide is not decomposed by lime, whilst it would be so by soda †. If, instead of the solution, the

* Journ. Soc. Chem. Ind. 1883, p. 110.

† I cannot otherwise understand his expression—"Even if the ammoniacal salts are washed out and boiled with strong soda, the results will be too high,

oxide itself were directly boiled with lime or soda, very much nitrogenous matter would be split up and would also yield ammonia, which would falsify the test.

Properties of Ammonia and its technically important Salts.

Ammonia, NH_3.

Colourless gas, of pungent smell and sharp, alkaline taste. Common ammonia, from its admixture of organic bases (pyridine &c.), has a much more disagreeable smell than pure. Spec. grav. 0·5967 : 1 litre at 0° and 0·76 metre pressure weighs 0·7635 gram ; vapour-tension * :—

At	− 33°·7	= 1	atmosphere.
,,	− 5°	= 4	atmospheres.
,,	0°	= 4·8	,,
,,	+ 10°	= 6·5	,,
,,	+ 20°	= 8·8	,,

By pressure and cold it can be condensed into a mobile, colourless, and strongly refringent liquid of spec. grav. 0·6362 at 0°, which boils at − 33°·7, and solidifies at − 75° to a white crystalline mass.

Composition, 82·39 per cent. N, 17·61 per cent. H ; 2 vols. of gaseous NH_3 are formed from 3 vols. of H and 1 vol. of N.

Ammonia is decomposed into its elements by the electric discharge; the ordinary electric spark acts but slowly and incompletely, but the current of a Ruhmkorff coil effects the decomposition quickly and completely †. Ammonia can be ignited in a current of oxygen, and burns with a greenish flame.

Ammonia is decomposed by heat into its elements, but very slowly, especially when mixed with other gases. The conditions of this decomposition have been studied by several chemists, especially Deville; the most recent investigation is by Ramsay and Young (Journ. Chem. Soc. 1884, vol. xlv. p. 88). We quote their

owing to the sulphocyanides"—taken in conjunction with the preceding paragraph, where milk of lime is prescribed as the proper way of treating the liquor. But a simple experiment shows that milk of lime equally expels the ammonia from ammonium sulphocyanide.

* Bunsen, Poggend. Annal. vol. xlvi. p. 95.

† Buff and Hofmann, Liebig's Annalen, cxiii. p. 132.

results somewhat in detail, as the manufacture of ammonia and its recovery as a by-product from the coking of coal, from blast-furnaces, &c. is greatly influenced by this instability of ammonia at high temperatures.

The percentages of ammonia decomposed by heat under varying conditions of temperature, material of the vessel, &c. were as follows:—

(1) With a porcelain tube filled with broken pieces of porcelain:—

At 500° C.....	1·575	per cent.	decomposed.
„ 520°	2·53	„	„
„ 600°	18·28	„	„
„ 620°	25·58	„	„
„ 680°	35·01	„	„
„ 690°	47·71	„	„
„ 810–830°.....	69·50	„	„

(2) With an iron tube filled with broken pieces of porcelain:—

At 507–527°	4·15	per cent.	decomposed.
„ 600° (current very fast) ...	21·36	„	„
„ 600° (current much slower)	34·44	„	„
„ 628°	65·43	„	„
„ 676–695°	66·57	„	„
„ 730°	93·38	„	„
„ 780°	100·00	„	„

(3) With a plain glass combustion-tube, lying in the iron tube:—

At 780° ..... 0·24 per cent. decomposed.

(4) With a glass combustion-tube, filled with fragments of broken glass tubing:—

At 780° ..... 1·72 per cent. decomposed.

(5) With a glass tube filled with strips of ignited asbestos cardboard:—

At 520°	2·90	per cent.	decomposed.
„ 780°	100·00	„	„

(6) With a plain iron tube, no oxide of iron present:—

At 780° ..... 100 per cent. decomposed.

(7) With an iron tube partially oxidized, and therefore water formed:—

At 780° ..... 95 per cent. decomposed.

(8) With a glass tube containing several lengths of iron wire:—

At 760° ..... 75 per cent. decomposed.

(9) With a glass tube containing several lengths of copper wire:—

At 760° ..... 2·0 per cent. decomposed.

(10) With a glass tube filled with copper reduced from the oxide, to give a large surface:—

At 780° ..... 50·2 per cent. decomposed.

The results may be summed up as follows:—(1) Under the most favourable circumstances (with an iron or porcelain tube, or a glass tube containing asbestos) the temperature at which ammonia-gas begins to decompose lies a little below 500°. (2) In contact with a glass surface, the temperature at which decomposition begins is much higher. (3) The influence of the time of exposure is very great. (4) The nature of the surface of the containing-vessel exerts an enormous influence on the amount of decomposition. (5) The amount of decomposition is greater when the surface is increased.—The decomposition was never absolutely complete, just as Deville had found when decomposing ammonia by the electric spark; probably because N and H recombine to a very slight extent. Such a combination could not be traced by heating a mixture of dry nitrogen and hydrogen; when the gases were moist a trace of ammonia was formed, probably owing to the production of nascent hydrogen from water and red-hot iron.

Ammonia with red-hot coal gives ammonium cyanide and hydrogen:

$$2NH_3 + C = NH_4 . CN + 2H.$$

(This condition is always present in gas-retorts.)

Solutions of alkaline hypobromites expel all the nitrogen from ammonia and its salts. (Upon this fact is based the azotometer, proposed by Knop for estimating ammonia.) With dry carbon dioxide, dry NH_3 yields ammonium carbamate:

$$2NH_3 + CO_2 = CO\begin{matrix}NH_2\\ONH_4\end{matrix}.$$

If moisture be present, ammonium carbonate is also formed.

Ammonia is absorbed by the chlorides of silver, of calcium, and of zinc, forming compounds which are only decomposed by strong heat. It is absorbed, both from its aqueous solution and that of its salts, by clayey soil, but not by pure kaoline.

Ammonia is absorbed with avidity by water and by alcohol. 1 gram of water at 0° and 0·76 metre pressure absorbs* 1146 c. c. of ammonia-gas = 0·899 gram NH_3, at 10° only 0·679 gram, at 20° 0·526 gram, at 30° 0·403 gram, at 100° 0·074 gram. (Exact statements on the influence of pressure and temperature upon the solubility of ammonia in water are given by Roscoe and Dittmar, *loco citato*, and by Sims, Ann. Chem. Pharm. cxviii. p. 345.)

It was formerly assumed that the solutions of ammonia contained a hydrate of ammonium, $NH_4.OH$, analogous to the hydrates of potassium and sodium &c.; but although the chemical behaviour of liquor ammoniæ altogether favours such an assumption, the thermo-chemical and physical observations of J. Thomson and of D. Tommasi (Chem. Centralbl. vol. xv. p. 418) disprove the existence of ammonium hydrate.

Of the tables of specific gravity of aqueous ammonia we shall first give that by Carius, for the temperature of 14°.

NH_3.	Spec. grav.	NH_3.	Spec. grav.	NH_3.	Spec. grav.
per cent.		per cent.		per cent.	
36·0	0·8844	31·8	0·8934	27·6	0·9036
35·8	0·8848	31·6	0·8938	27·4	0·9041
35·6	0·8852	31·4	0·8943	27·2	0·9047
35·4	0·8856	31·2	0·8948	27·0	0·9052
35·2	0·8860	31·0	0·8953	26·8	0·9057
35·0	0·8864	30·8	0·8957	26·6	0·9063
34·8	0·8868	30·6	0·8962	26·4	0·9068
34·6	0·8872	30·4	0·8967	26·2	0·9073
34·4	0·8877	30·2	0·8971	26·0	0·9078
34·2	0·8881	30·0	0·8976	25·8	0·9083
34·0	0·8885	29·8	0·8981	25·6	0·9086
33·8	0·8889	29·6	0·8986	25·4	0·9094
33·6	0·8894	29·4	0·8991	25·2	0·9100
33·4	0·8898	29·2	0·8996	25·0	0·9106
33·2	0·8903	29·0	0·9001	24·8	0·9111
33·0	0·8907	28·8	0·9006	24·6	0·9116
32·8	0·8911	28·6	0·9011	24·4	0·9122
32·6	0·8916	28·4	0·9016	24·2	0·9127
32·4	0·8920	28·2	0·9021	24·0	0·9133
32·2	0·8925	28·0	0·9026	23·8	0·9139
32·0	0·8929	27·8	0·9031	23·6	0·9145

* Roscoe and Dittmar, Ann. Chem. Pharm. cxii. p. 349.

Table (*continued*).

NH_3.	Spec. grav.	NH_3.	Spec. grav.	NH_3.	Spec. grav.
per cent.		per cent.		per cent.	
23·4	0·9150	15·6	0·9393	7·8	0·9677
23·2	0·0156	15·4	0·9400	7·6	0·9685
23·0	0·9162	15·2	0·9407	7·4	0·9693
22·8	0·9168	15·0	0·9414	7·2	0·9701
22·6	0·9174	14·8	0·9420	7·0	0·9709
22·4	0·9180	14·6	0·9427	6·8	0·9717
22·2	0·9185	14·4	0·9434	6·6	0·9725
22·0	0·9191	14·2	0·9441	6·4	0·9733
21·8	0·9197	14·0	0·9449	6·2	0·9741
21·6	0·9203	13·8	0·9456	6·0	0·9749
21·4	0·9209	13·6	0·9463	5·8	0·9757
21·2	0·9215	13·4	0·9470	5·6	0·9765
21·0	0·9221	13·2	0·9477	5·4	0·9773
20·8	0·9227	13·0	0·9484	5·2	0·9781
20·6	0·9233	12·8	0·9491	5·0	0·9790
20·4	0·9239	12·6	0·9498	4·8	0·9799
20·2	0·9245	12·4	0·9505	4·6	0·9807
20·0	0·9251	12·2	0·9512	4·4	0·9815
19·8	0·9257	12·0	0·9520	4·2	0·9823
19·6	0·9264	11·8	0·9527	4·0	0·9831
19·4	0·9271	11·6	0·9534	3·8	0·9839
19·2	0·9277	11·4	0·9542	3·6	0·9847
19·0	0·9283	11·2	0·9549	3·4	0·9855
18·8	0·9289	11·0	0·9555	3·2	0·9863
18·6	0·9296	10·8	0·9563	3·0	0·9873
18·4	0·9302	10·6	0·9571	2·8	0·9882
18·2	0·9308	10·4	0·9578	2·6	0·9890
18·0	0·9314	10·2	0·9586	2·4	0·9899
17·8	0·9321	10·0	0·9593	2·2	0·9907
17·6	0·9327	9·8	0·9601	2·0	0·9915
17·4	0·9333	9·6	0·9608	1·8	0·9924
17·2	0·9340	9·4	0·9616	1·6	0·9932
17·0	0·9347	9·2	0·9623	1·4	0·9941
16·8	0·9353	9·0	0·9631	1·2	0·9950
16·6	0·9360	8·8	0·9639	1·0	0·9959
16·4	0·9366	8·6	0·9647	0·8	0·9967
16·2	0·9373	8·4	0·9654	0·6	0·9975
16·0	0·9380	8·2	0·9662	0·4	0·9983
15·8	0·9386	8·0	0·9670	0·2	0·9991

The following table by Wachsmuth (Wagner's Jahresb. 1876, p. 447) refers to a temperature of 12° C.

Specific gravity at 12°.	1 kilog. contains of NH_3	1 litre contains of NH_3	1 litre consists of	
			water.	liquid ammonia.
	grams.	grams.	cub. centim.	cub. centim.
0·870	384·4	334·5	535·5	464·5
0·872	376·9	328·6	543·4	456·6
0·874	369·4	322·8	551·2	448·8
0·876	362·0	317·1	558·9	441·1
0·878	354·6	311·3	566·7	433·3
0·880	347·2	305·5	574·5	425·5
0·882	340·0	299·8	582·2	417·8
0·884	332·9	294·2	589·8	410·2
0·886	325·8	288·6	597·4	402·6
0·888	318·7	283·0	605·0	395·0
0·890	311·6	277·3	612·7	387·3
0·892	304·7	271·7	620·3	379·7
0·894	297·8	266·2	627·8	372·2
0·896	290·9	260·6	635·4	364·6
0·898	284·1	255·1	642·9	357·1
0·900	277·3	249·5	650·5	349·5
0·902	270·7	244·1	657·9	342·1
0·904	264·1	238·7	665·3	334·7
0·906	257·7	233·4	672·6	327·4
0·908	251·3	228·2	679·8	320·2
0·910	244·9	222·8	687·2	312·8
0·912	238·6	217·6	694·4	305·6
0·914	232·3	212·3	701·7	298·3
0·916	226·0	207·0	709·0	291·0
0·918	219·7	201·6	716·4	283·6
0·920	213·4	196·3	723·7	276·3
0·922	207·3	191·1	730·9	269·1
0·924	201·2	185·9	738·1	261·9
0·926	195·1	180·6	745·4	254·6
0·928	189·0	175·4	752·6	247·4
0·930	182·9	170·1	759·9	240·1
0·932	176·9	164·8	767·2	232·8
0·934	170·9	159·6	774·4	225·6
0·936	164·9	154·3	781·7	218·3
0·938	158·9	149·0	789·0	211·0
0·940	152·9	143·7	796·3	203·7
0·942	147·1	138·5	803·5	196·5
0·944	141·3	133·3	810·7	189·3
0·946	135·6	128·2	817·8	182·2
0·948	129·9	123·1	824·9	175·1
0·950	124·2	118·0	832·0	168·0
0·952	118·7	113·0	839·0	161·0
0·954	113·2	108·0	846·0	154·0
0·956	107·8	103·0	853·0	147·0
0·958	102·4	98·1	859·9	140·1
0·960	97·0	93·1	866·9	133·1
0·962	91·6	88·1	873·9	126·1
0·964	86·2	83·0	881·0	119·0
0·966	80·8	78·0	888·0	112·0
0·968	75·5	73·0	895·0	105·0
0·970	70·2	68·0	902·0	98·0
0·972	65·2	63·6	908·7	91·3
0·974	60·2	58·6	915·4	84·6

Table (*continued*).

Specific gravity at 12°.	1 kilog. contains of NH_3	1 litre contains of NH_3	1 litre consists of	
			water.	liquid ammonia.
	grams.	grams.	cub. centim.	cub. centim.
0·976	55·2	53·8	922·2	77·8
0·978	50·2	49·1	928·9	77·1
0·980	45·3	44·3	935·7	64·3
0·982	40·4	39·6	942·4	57·6
0·984	35·5	34·9	949·1	50·9
0·986	30·6	30·1	955·9	44·1
0·988	25·8	25·5	962·5	37·5
0·990	21·0	20·7	969·3	30·7

An investigation made in my laboratory by J. H. Smith* has proved that the numbers given by Carius are more accurate than those by Wachsmuth, leaving aside the totally incorrect tables of previous authors (Ure, Dalton, Davy), which ought never to be used at all.

Ammonium carbonate †.

Several of the compounds of carbonic acid and ammonia formerly assumed to be present are not acknowledged now, and only those mentioned below are so. They are all decomposed at 58–60° into carbon dioxide, ammonia, and water respectively; hence they do not exist as compounds in the gas while hot, but are only formed on its cooling.

Neutral salt, $(NH_4)_2CO_3,H_2O$ (first described by Divers).—Lengthened plates; smells and tastes like ammonia; deliquesces in the air with formation of acid salt, losing ammonia and water; splits up at 58° into water, carbon dioxide, and ammonia. When it is dissolved in water, it can be recrystallized unchanged by cooling; but the dilute aqueous solution, according to some, already contains a mixture of free ammonia and neutral and acid ammonium carbonate. (This statement is denied by Divers.) The aqueous solution begins to give off gas at 70° or 75°, boils at 75° or 80°, and

* Journ. Soc. Chem. Ind. 1883, p. 80.

† An extensive memoir on the combinations of carbonic anhydride with ammonia and water has been published by E. Divers (Journ. Chem. Soc. 1870, vol. viii. p. 171). The following statements are to a great extent based on that memoir, and are supplemented by private communications, kindly made to the author by Dr. Divers, which partly rectify the extracts from Gmelin-Kraut's Handbook, given in the first edition of this work.

gives off CO_2 and NH_3 in the same proportion as they exist in the salt.

Semiacid salt, $(NH_4)_4H_2(CO_3)_3,H_2O$.—Thin hexagonal plates; smell and taste of ammonia. Decomposed by a little water; dissolves unchanged in 5 parts of water at 15°, which solution rapidly evolves gas when heated (*Divers*).

Acid salt, $(NH_4)H(CO_3)$ = ammonium bicarbonate.—Is found ready formed in many guano beds &c., also frequently in gas-purifiers, pipes, &c. This salt is usually assumed to exist in gas-liquor; but some assert that the other carbonates occur there as well. Some of the "commercial" carbonate of ammonia recently manufactured in England is nothing but the bicarbonate, as proved by the analyses of Hanekop (Archiv der Pharmacie, 1886, vol. xxiv. p. 21) and Reissmann (Pharm. Centralhalle, 1886, p. 105). It is always formed when the other salts richer in ammonia or ammonium carbamate effloresce. According to Divers, the condition for its formation seems to be the introduction of water-vapour and ammonia in atomic proportions into carbonic anhydride, so slowly that the water is never in sufficient quantity to condense to the liquid state; a warm condenser, therefore, is favourable to it. It occurs as a white mealy powder or as rhombic crystals, mostly columnar. Sp. gr. 1·573 (Schiff); the natural one = 1·45 (Ulex). In the dry state it does not smell of ammonia; it tastes cooling and saline. In dry air it is stable; in moist air the crystals lose their brilliancy. At 60° it slowly decomposes into CO_2, NH_3, and H_2O. It readily dissolves in water; in the air the solution rapidly loses carbonic acid, and on being gently heated gives off gas-bubbles, a salt richer in ammonia remaining behind. According to Dibbits*, 100 parts of water dissolve

At 10°	10°	15°	20°	25°	30°
11·9	15·8	18·3	21·0	23·9	27·0 parts of salt.

Ammonium carbamate (formerly called dry ammonium carbonate), $CO\langle^{NH_2}_{ONH_4}$, hence forming the intermediate term between neutral ammonium carbonate, $CO\langle^{ONH_4}_{ONH_4}$, and carbamide or urea, $CO\langle^{NH_2}_{NH_2}$. It is always formed when ammonia and carbon dioxide meet nearly in the dry state and not too hot, and even in the presence of moisture if at least 2 vols. NH_3 are present to 1 vol.

* Dingler's Journal, ccxvi. p. 164.

CO_2; hence it is a principal component of commercial ammonium carbonate, and can be obtained from this by slow distillation &c. It occurs in prisms or crystalline laminæ or crystalline crusts, smells strongly of ammonia, deliquesces in the air, and almost completely volatilizes.

The vapour-tensions of ammonium carbamate are (in millimetres)*:—

At 0°, 12·4	At 30°, 124	At 54¾°, 563
„ 10°, 29·8	„ 40°, 248	„ 56°·5, 632
„ 20°, 62·4	„ 47¼°, 361	

The vapours consist of a mixture of NH_3 and CO_2.

At 59° or 60° it decomposes entirely into CO_2 and $2NH_3$; at 50° or 55° it is reformed from these components. It dissolves in 1½ part of water with considerable absorption of heat, and is then quickly converted into the acid salt, ammonia being given off.

Commercial carbonate of ammonia, salt of hartshorn, sal volatile, is a mixture of ammonium bicarbonate and ammonium carbamate, usually containing a little adhering water. It is formed from a mixture of carbon dioxide (even in excess) and ammonia-gas in the presence of sufficient aqueous vapour. According to the opinion once generally entertained, it is also formed in the quick distillation of any of the ammonium carbonates, or of ammonium chloride or sulphate with chalk; but Divers has proved that in this case the neutral carbonate is formed, and this is only converted into the "commercial" carbonate in the process of redistillation (sublimation). Experiments recently made in my own laboratory have entirely confirmed Divers's observation. In all these cases no doubt CO_2, NH_3, and H_2O must be assumed to exist free while in the state of vapour. Formerly the commercial salt had the formula

$$2(NH_4)HCO_3, CO(NH_2)(ONH_4),$$
$$= 28{\cdot}81\,NH_3, 55{\cdot}96\,CO_2, 15{\cdot}25\,H_2O;$$

when gently heated in a retort it gradually liquefied, and dissolved

At 13°	16°·7	32°	40°·6	49°	
in 4	3·3	2·7	2·4	2	parts of water.

Divers has proved that the salt analyzed by him (in 1870) was richer in ammonia, according to the formula

$$(NH_4)HCO_3, CO(NH_2)(ONH_4),$$

corresponding to 32·48 NH_3, 56·05 CO_2, and 11·47 H_2O.

* Naumann, Berichte, 1871, p. 783; Erckmann, ibid. 1885, p. 1157.

It remains solid on heating; in the air it effloresces, losing 47 per cent. by weight, and leaving friable ammonium bicarbonate behind (of which the commercial salt now sometimes consists altogether, comp. p. 586). The same is left when the salt is treated with a small quantity of water.

It dissolves at 15° in 4 parts of water, with considerable absorption of heat, at 65° in 1½ part. At 75° the solution begins to give off much CO_2, at 85° also ammonia; at 100° all the salt is volatilized. In dilute solutions the liberation of the salt takes place later on (*Divers*).

Vogler * also considers commercial carbonate of ammonia to be a compound of acid ammonium carbonate with ammonium carbamate. His observations exceed those of Divers only by a direct estimation of the combined water.

According to information, received from one of the largest German ammonia manufacturers, there are both qualities of carbonate of ammonia found in commerce, that with about 30 per cent. NH_3 (approaching Divers's formula) and that with about 25 per cent. NH_3. Their value as baking-powders is about the same. The acid carbonate (with 21·5 per cent. NH_3) is but little made.

The specific gravity of the solutions of commercial ammonium carbonate has been determined by J. H. Smith, with my co-operation †. The salt experimented on had the composition—31·3 per cent. NH_3, 56·6 per cent. CO_2, 12·1 per cent. H_2O, which

Degrees Twaddell.	Spec. grav. at 15°.	Per cent. ammon. carbonate.	Spec. grav. Factor for 1° C.	Degrees Twaddell.	Spec. grav. at 15°.	Per cent. ammon. carbonate.	Spec. grav. Factor for 1° C.
1	1·005	1·66	0·0002	16	1·080	23·78	0·0006
2	1·010	3·18	0·0002	17	1·085	25·31	0·0006
3	1·015	4·60	0·0003	18	1·090	26·82	0·0007
4	1·020	6·04	0·0003	19	1·095	28·33	0·0007
5	1·025	7·49	0·0003	20	1·100	29·93	0·0007
6	1·030	8·93	0·0004	21	1·105	31·77	0·0007
7	1·035	10·35	0·0004	22	1·110	33·45	0·0007
8	1·040	11·86	0·0004	23	1·115	35·08	0·0007
9	1·045	13·36	0·0005	24	1·120	36·88	0·0007
10	1·050	14·83	0·0005	25	1·125	38·71	0·0007
11	1·055	16·16	0·0005	26	1·130	40·34	0·0007
12	1·060	17·70	0·0005	27	1·135	42·20	0·0007
13	1·065	19·18	0·0005	28	1·140	44·29	0·0007
14	1·070	20·70	0·0005		1·1414	44·90	0·0007
15	1·075	22·25	0·0006				

* Zeitschr. für anal. Chemie, xvii. p. 451.

† Journ. Soc. Chem. Ind. 1883, p. 80.

most nearly approaches Divers's formula. The Table annexed shows the specific gravity at 15° and the factor for reducing the specific gravities, found at other temperatures, to 15°.

Suppose we have found a spec. grav. of 1·108 at 19°, we shall take that at $15° = 1·108 + 0·0007\ (19-15) = 1·1108 = 33·71$ per cent. ammonium carbonate.

Ammonium sulphide.

There exist a monosulphide, $(NH_4)_2S$, a sulphhydrate, NH_4SH, and several polysulphides, containing from 2 to 7 atoms of S to 2 molecules of NH_4. They are all volatile, soluble in water, and easily decomposable.

Ammonium monosulphide, $(NH_4)_2S$, is formed from hydrogen sulphide and ammonia in excess. At −18° colourless shining crystals, dissolving readily and without colour in water. This solution is stable, whilst the crystals in the air at once lose half their ammonia. In the state of vapour it cannot exist, but dissociates into NH_3 and H_2S.

Ammonium sulphhydrate, NH_4SH, is formed by passing hydrogen sulphide into liquor ammoniæ to saturation (the ordinary laboratory reagent). The originally colourless solution soon turns yellow in the air, polysulphides being formed. Below −10° it can be crystallized; on evaporation it dissociates into H_2S and NH_3. On prolonged contact with air the solution deposits sulphur, and ammonium thiosulphate is formed.

The polysulphides are also prepared by dissolving sulphur in ordinary ammonium sulphide.

Ammonium sulphide has not hitherto been manufactured on a large scale; but this might be done, according to Spence, by mixing in a retort sulphate of ammonia with alkali waste or spent gas-lime (both of them very rich in calcium sulphide), blowing in steam, and passing the vapours into a condensing-apparatus. Care must, however, be taken lest the pipes be stopped up by solidifying ammonium sulphide.

Ammonium sulphocyanide (thiocyanate), NH_4CNS.

Colourless shining scales, without water of crystallization; that crystallized from an aqueous solution is somewhat deliquescent; that from alcohol is stable in the air. Very soluble in water, with considerable lowering of the temperature, and in alcohol. On heating the dry salt it fuses at 145–160°, and decomposes

soon after. Consequently it cannot exist in the state of vapour, but is only formed on cooling from ammonium sulphide and carbon bisulphide,

$$(NH_4)_2S + CS_2 = NH_4,NCS + 2H_2S,$$

or else from ammonium cyanide and sulphide. In English gas-liquors from 3 to 5 ounces of ammonium sulphocyanide per gallon is found. It is also found in considerable quantities in the spent oxide of iron of the gas-purifiers.

Ammonium cyanide, NH_4,CN.

A colourless salt, crystallizing in cubes, smelling and tasting both of prussic acid and ammonia, with an alkaline reaction, as poisonous as prussic acid. It is very soluble in water and alcohol; it is very volatile, boiling, according to some chemists, at 36°; but, from its vapour-density, it must be assumed to undergo dissociation into ammonia and prussic acid. The dry salt is very unstable, and in the air is quickly converted into a brown nitrogenous substance (azulmic acid).

Ammonium chloride (*Sal-ammoniac*), NH_4Cl.

Known from ancient times; also ready formed in nature, especially in volcanic districts, and in the vicinity of coal-fields. In the pure state without colour or taste. Crystallizes from water or alcohol in octahedra arranged in the form of feathers, from urea in cubes. Sublimed sal-ammoniac consists of fritted fibrous crystalline masses. It is very tough and difficult to powder. Sp. gr. 1·52. Soluble in water with much absorption of heat. 100 parts of water dissolve

At 0°	10°	110°
28·4	32·8	77·2 parts.

Specific gravity of Solutions of Ammonium Chloride at 15°.

Per cent.	Spec. grav.	Per cent.	Spec. grav.	Per cent.	Spec. grav.
1	1·00316	10	1·03081	19	1·05648
2	1·00632	11	1·03370	20	1·05929
3	1·00948	12	1·03658	21	1·06204
4	1·01264	13	1·03947	22	1·06479
5	1·01580	14	1·04325	23	1·06754
6	1·01880	15	1·04524	24	1·07029
7	1·02180	16	1·04804	25	1·07304
8	1·02481	17	1·05086	26	1·07375
9	1·02781	18	1·05367		

Ammonium chloride is not volatile at the ordinary temperature. On being heated it evaporates without fusing, and sublimes in crusts (as above mentioned). Its vapour is a dissociated mixture of NH_3 and HCl. On boiling its aqueous solution a little ammonia escapes, and the reaction becomes distinctly acid; hence it strongly acts upon metal (especially iron) vessels, and is contaminated itself. Even in the neutral state ammonium chloride in the presence of water acts strongly upon iron, copper, &c., and promotes the corrosion of these metals.

Ammonium sulphate.

Of the different sulphates of ammonia we are only interested in the *neutral*, $(NH_4)_2SO_4$, which occurs in transparent rhombic crystals, isomorphous with potassium sulphate. The native ammonium sulphate found in the volcanic regions of South Italy is called *mascagnine*. Sp. gr. 1·76; bitter, acrid taste; decrepitates on being heated, fuses at 140°, and begins to decompose at 280°; it cannot be volatilized without change. 100 parts of water dissolve at

0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
71·0	73·65	76·3	78·95	81·6	84·25	86·9	89·55	92·2	93·85	97·5

parts of the salt. In absolute alcohol it is insoluble.

Specific gravity of the Solutions of Ammonium Sulphate at 15° C.

Per cent.	Spec. grav.	Per cent.	Spec. grav.	Per cent.	Spec. grav.
1	1·0057	18	1·1035	35	1·2004
2	1·0112	19	1·1092	36	1·2060
3	1·0172	20	1·1149	37	1·2116
4	1·0230	21	1·1207	38	1·2172
5	1·0287	22	1·1265	39	1·2228
6	1·0345	23	1·1323	40	1·2284
7	1·0403	24	1·1381	41	1·2343
8	1·0460	25	1·1439	42	1·2402
9	1·0518	26	1·1496	43	1·2462
10	1·0575	27	1·1554	44	1·2522
11	1·0632	28	1·1612	45	1·2583
12	1·0690	29	1·1670	46	1·2644
13	1·0747	30	1·1724	47	1·2705
14	1·0805	31	1·1780	48	1·2766
15	1·0862	32	1·1836	49	1·2828
16	1·0920	33	1·1892	50	1·2890
17	1·0977	34	1·1948		

CHAPTER XIV.

THE WORKING-UP OF AMMONIACAL LIQUOR.

Storing and Settling-out of the Tar.

ACCORDING to the nature of things, ammoniacal liquor, such as results from mixing up the aqueous liquids from the hydraulic main, condensers, and scrubbers, is always more or less charged with tarry substances. Some of these are actually dissolved in the water; but others are only present in the state of suspension, and can be separated by proper settling. It is very important that this really should be done, as the nuisance connected with working ammoniacal liquor is very much lessened by the removal of those tarry substances.

An excellent arrangement for this purpose has been made at the Vaugirard gas-works at Paris, where formerly the complaints of the neighbours were very strong. It is shown in figs. 146 and 147, in vertical section and ground-plan. The gas-liquor is stored in large underground brickwork cisterns, GG, and is from these pumped by pumps TT (driven by the steam-engine M) into the four iron tanks, B, C, D, E, mounted at a height. These tanks communicate by overflows; the liquor is first pumped into B, and from there gradually gets into C, D, and E. During this passage the settling down of the tar takes place. Most of it is found in B and C, very little in the others. The liquor, now practically free from tar, runs away from the surface of the last settler, E, through the pipe, S, into the gauging-tank, from which the stills are charged. The tar collecting at the bottom of the two first settlers, B, C, is drawn off by the cock F, and run into iron tank-waggons, to be transported to the tar-works. The small quantity

Fig. 146.

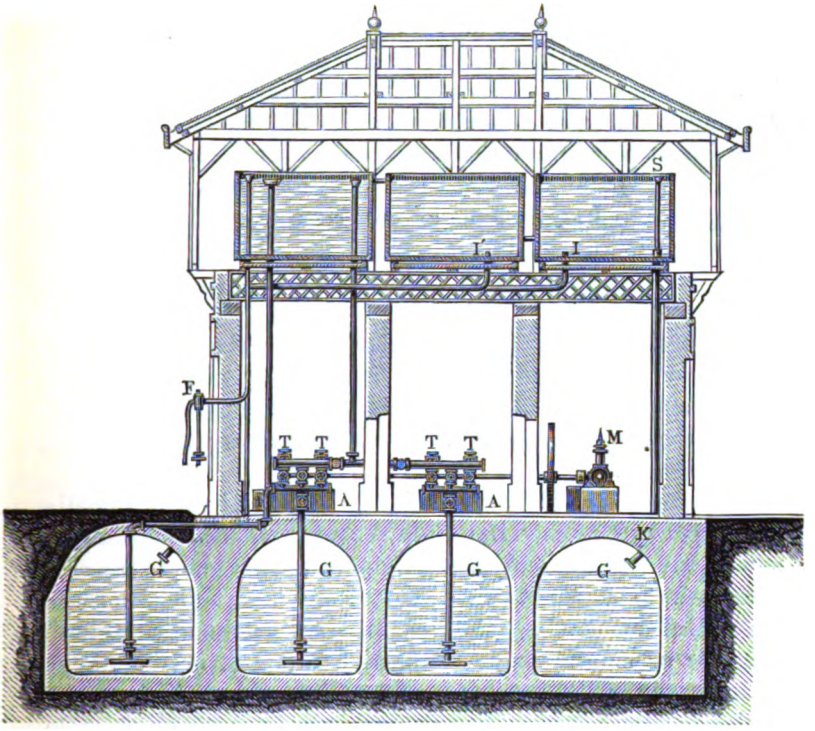
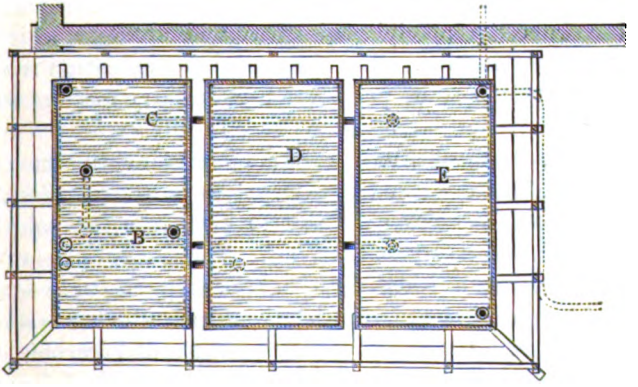


Fig. 147.



of tar collecting in D and E is run back into the cisterns G G by means of the pipes I, I′, and K.

If gas-liquor has to be kept in stock for any length of time, it must not be forgotten that it loses a good deal of its ammonia by evaporation. This loss may be to a great extent avoided by running in the fresh liquor near to the bottom of the tank, and pumping it away from the same place. Thus the upper portion of the contents of the tanks remains very nearly unchanged for a long time, and protects the lower portion from a loss of ammonia by evaporation.

Working-up Gas-liquor without Distillation.

The working-up of gas-liquor has for its aim mostly the production of ammonium sulphate; more rarely that of liquor ammoniæ, and even still more rarely that of ammonium chloride (sal-ammoniac). Ammonium carbonate is mostly made indirectly from sulphate.

The conversion of raw gas-liquor into sulphate is sometimes performed by bringing it in contact with *calcium sulphate* (gypsum); but this gives only a very impure article, and, cheap as this plan seems to be, is not carried out by any large number of works.

Al. McDougall (B. P. 202, 1882) mixes calcium or magnesium sulphate or chloride with sawdust, bark, peat, or the like, and sprinkles the gas-liquor over it, after having added a little sulphuric or hydrochloric acid. Thus ammonium sulphate or chloride is produced.

De la Martellière (B. P. 2963, 1880) adds to gas-liquor aluminium sulphate, and draws off the resulting solution of ammonium sulphate from the precipitated silica and alumina, which carry down the tarry matters. The purport of this invention is not very clear, since this sort of purification from tarry matters would be rather expensive.

Formerly, the most usual process of treating so much of the gas-liquor as was not run to waste was to *saturate it directly with sulphuric or hydrochloric acid,* and to evaporate the solution till the ammonium salt crystallized out. The gases escaping at the saturation, carbon dioxide and hydrogen sulphide, were sometimes passed through a fire to burn the latter gas, which was done very imperfectly, owing to the admixed moisture and carbon dioxide. The resulting sulphate or chloride of ammonia was very much

discoloured by tarry substances, and would now-a-days be hardly saleable. Apart from this, direct saturation must be pronounced to be irrational, because the evaporation of such dilute solutions takes more fuel than the driving-off of ammonia in properly constructed apparatus; and there is, moreover, a smell of H_2S during the concentration of the liquors. Direct saturation seems to be but rarely, if at all, practised now for sulphate, but it is still done for ammonium chloride.

Sometimes crude gas-liquor is *directly used as manure*; but its carriage would form an obstacle to a more extended employment of this kind, and the inevitable loss of ammonia by evaporation is also an impediment to it.

Manufacture of Sulphate of Ammonia by distilling Gas-liquor.

Boiling with or without Lime.

A great part of the ammonia in gas-liquor (in good liquor most of it) is present in the form of salts which volatilize on boiling, although with dissociation—essentially ammonium carbonate and sulphide. This "volatile" ammonia can be expelled by simple prolonged boiling of the liquor; but the "fixed" ammonia—that is, that present as sulphate, chloride, sulphocyanide, &c.—remains behind in that case, and can only be expelled by *decomposing the salts with lime.*

We have seen (p. 566 *et seq.*) that the proportion between "volatile" and "fixed" ammonia varies greatly. In very good liquors only a small percentage of the ammonia is "fixed;" and in such cases the treatment with lime, which complicates the apparatus and process and greatly prolongs the boiling, does not seem to pay, Hence many (especially English) manufacturers never use any lime in their ammonia-stills (according to Dr. Ballard's Report, p. 129, this is only a minority even among English ammonia-makers).

This, however, ought never to be done if the "fixed" ammonia exceeds a very few per cent. of the total ammonia. Although even by the lime treatment the latter is rarely absolutely set free and utilized, yet the additional ammonia gained by that treatment pays very well for the process if it amounts to at least something like 5 per cent.; and this is probably the general case with

gas-liquors mixed from all parts of the condensing- and scrubbing-plant.

J. H. Cox (comp. p. 567) considers it a good rule to add 50 lb. of lime per 1000 gallons for every 100 grains of fixed ammonia per gallon of the liquor, that is, 350 lime to 100 fixed ammonia. In practice it is easy, by analyzing the products of manufacture, to arrive at the proper quantity of lime to add, which, of course, is always greatly in excess of the theoretical.

In an apparatus, consisting of two stills (in the second of which lime was used), J. Hepworth (Journal of Gas-Lighting, Oct. 1883) found the following strengths of liquor:—

As run into No. 1 still	2·540	per cent. NH_3
„ „ No. 2 still	0·589	„ „
As taken from No. 2 still ...	0·068	„ „

The difference between the two latter tests represents the "fixed" ammonia recovered by lime.

According to the general experience of German gas-works, the fixed ammonia on an average amounts to one fifth of the total ammonia.

In any case, all apparatus are so contrived that first the volatile ammonium salts are expelled by heat alone, before lime is added to decompose the fixed salts—at any rate, when the production of sulphate is aimed at. Since in all practical cases an excess of lime must be employed, there is always some trouble from crusts of calcium hydrate, and even of calcium salts, firmly adhering to the bottom and sides of the still. This is especially awkward with stills heated by direct fire, and is probably the principal cause why so many sulphate manufacturers forego the recovery of the fixed ammonia; but that drawback may be said to have been entirely overcome by the stills of Grüneberg, Feldmann, P. Mallet, and other modern inventions to be described later on.

It is generally assumed that the moment an ammonium salt (say ammonium chloride) and calcium hydrate meet, ammonia is set free and calcium chloride is formed. This is contradicted by Isambert*, who argues that the reaction

$$2NH_4Cl + CaO = CaCl_2 + 2NH_3 + H_2O$$

absorbs heat to the amount of 10·9 calories; if the lime is used in

* Compt. Rend. vol. c. p. 857.

the caustic state, 7·55 calories should be deducted for the previous formation of $Ca(OH)_2$. Hence at "ordinary" temperatures no ammonia is set free, even *in vacuo*; but the compound $CaCl_2(NH_3)_2$ is formed, in the formation of which 14 calories are evolved, and which gives off its ammonia at 180°–200°. This is also the case with baryta and strontia, but not with lead oxide.

Without entering upon a discussion as to the validity of these theoretical considerations, it must be stated that certainly a considerable amount of boiling is necessary to expel all the ammonia from the above mixture; that this can be done only by prolonged treatment in the hot state (p. 574); and that it is much better done in dilute than in concentrated liquors. Usually the treatment in practical working is not continued up to the point where all ammonia is expelled. Cox (*loc. cit.*) states that at the works he manages the liquor contained 15 per cent. of its total ammonia combined as fixed salt, and that by the lime treatment 5 per cent. of this was recovered, 10 per cent. going to waste; but this is decidedly far more than need be lost. At the same meeting Hepworth quoted his own case, in which, of the total ammonia, 76·9 per cent. was expelled by boiling alone, 20·5 by treatment with lime, and only 2·6 remained in the waste liquor; and even this (apparent) final loss would probably in reality be less, as caustic soda had been employed for testing, by which some of the cyanides were decomposed. At most German works, also, the loss of ammonia in the waste liquors (as we shall see when describing Grüneberg's and Feldmann's stills) is quite insignificant. The best proof that Mr. Cox's figures do not represent by far the ordinary state of the case is afforded by the daily practice of ammonia-soda works, whose ammonia is mostly "fixed," and which could not exist if they lost anything like that portion of NH_3 in their waste liquors.

Sometimes the distillation with lime causes a very awkward frothing. This, according to the Société anonyme des produits chimiques du Sud-Ouest (G. P. 18773), is caused by calcium carbonate in a state of suspension. It is therefore proposed first to drive off the volatile ammonia, and then slightly to acidulate the liquor before adding lime.

Magnesia is sometimes used in lieu of lime for decomposing salts of ammonia; but, apart from analytical purposes, only in such cases when it is intended to recover the chlorine of ammonium

chloride—a problem incessantly attacked, but not yet sufficiently solved, in the manufacture of soda by the ammonia process. It is, of course, an indispensable condition that the magnesia must be recovered, as its price prohibits wasting it like lime. The details of the many attempts made in this direction do not belong to the chapter on Ammonia manufacture, but to that on Alkali manufacture. We will therefore only briefly mention a very important patent of Messrs. Pechiney & Co. (B. P. 9927, 1885). They found that the decomposition of solutions of ammonium chloride by magnesia, even at the boiling temperature, is only complete when the liquor is kept in a certain state of concentration, and they have accordingly constructed a still in which no steam is condensed, and no separation of NH_3 and water takes place, till the decomposition has been entirely accomplished. Only then the usual dephlegmation comes into play.

Mode of Heating the Stills.

The apparatus for distilling gas-liquor differ in the way of heating. This may be done either by a direct fire, or by open (wet) steam, or by indirect (dry) steam. Sometimes superheated steam is also employed. Expelling the ammonia by boiling alone, without employing the sensible and latent heat of the vapours evolved, consumes very much time and fuel. Hence in all the modern apparatus that heat is utilized for a preliminary heating of fresh gas-liquor, and for driving out the volatile ammonia, and at the same time the gas is freed from aqueous vapour by dephlegmation. The additional first cost of a properly constructed apparatus is soon paid for by an enormous saving in fuel. An exceedingly large variety of types of apparatus have been devised for this purpose, a number of which will be described in detail later on; their principle is always the same as that carried out in rectifying spirit of wine or light tar-oils (p. 462 *et seq.*).

Which kind of heating is most advantageous for distilling ammonia seems to be decided by the following experiments on a manufacturing scale, made by Dr. C. M. Tidy. A quantity of gas-liquor, amounting to 7000 gallons, requires—

	Hours.	Yields, as compared with the theory.
When heated by open fire from without...	22	90 per cent.
„ „ indirect steam (in a coil) .	18	92 „
„ „ open (wet) steam	14	98·5 „

This proves that steam directly blown into the liquor is by far the best agent, no doubt because its heat is thus most directly utilized, and perhaps even more so because the steam mechanically carries away the ammonia.

Safety-valves.

All stills intended for expelling ammonia without lime ought to be provided with safety-valves—a precaution not unfrequently neglected. The gas-delivery pipes easily get plugged up by ammonium carbonate, and this may lead to dangerous explosions. Seidel (in Hofmann's Report on the Vienna Exhibition, vol. i. p. 96) and Watson Smith (private communication) testify to this. Danger is avoided by fitting up the boilers with safety-valves.

Absorbing the Vapours in Sulphuric Acid.

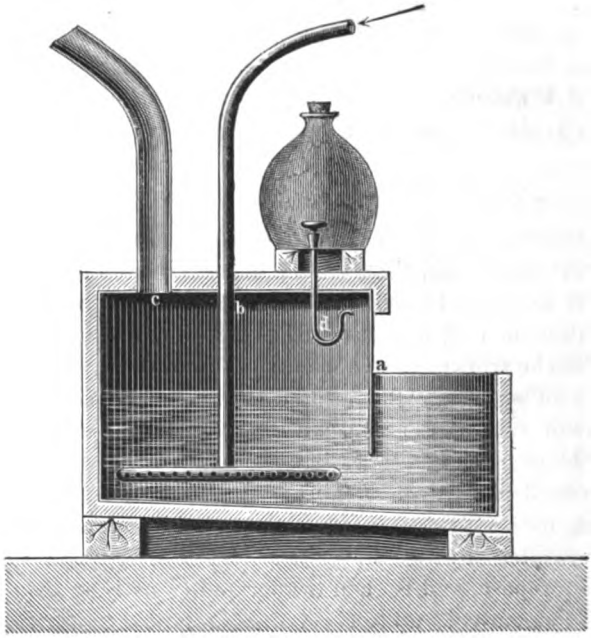
The apparatus intended for this purpose, called the *saturator*, must be so constructed that, on the one hand, no ammonia escapes absorption in the acid, and, on the other hand, the gases set free (carbon dioxide and sulphuretted hydrogen) do not become injurious to the workmen and the neighbourhood. In explaining a number of special apparatus we shall meet with various constructions of saturators; here we only mention the general principles to be observed.

In one kind of saturators the gas, partly or mostly dehydrated by dephlegmation, is condensed in *dilute* sulphuric acid, so that no salt is separated during the saturation; the solution formed is clarified by repose, and is then evaporated (mostly in lead pans by means of a steam-coil) up to crystallization, during which operation an offensive smell is given off. The mother-liquor is employed for diluting a fresh quantity of sulphuric acid. In another kind of saturators the ammoniacal vapours are absorbed in somewhat *concentrated* sulphuric acid (say 140° Tw.), in which case the ammonium sulphate separates in the solid state in the saturating-vessels,

and is fished out from them from time to time. More acid is run in continuously, in a thin jet, so that the saturator is always kept filled up to about the same level. The second process has the advantage of being continuous and saving all evaporation, but possesses the drawback that the liquor cannot clarify, and the salt does not come out so pure as in the first process.

The saturators differ in form as follows:—That intended for dilute acid is a closed tank lined with lead, partially filled with sulphuric acid at 80°–100° Tw.; the ammoniacal vapours arrive in a pipe, which branches out at the bottom of the tank, and is there provided with many holes for the issue of the ammoniacal vapours. The gases liberated by the decomposition, along with a large quantity of steam generated by the heat of the reaction,

Fig. 148.

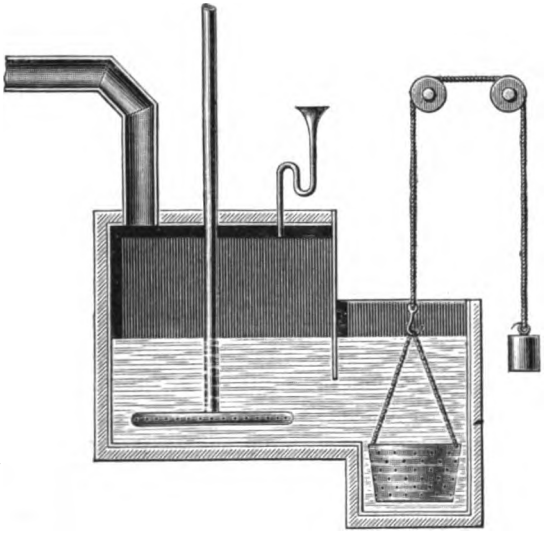


are conducted away by a pipe from the upper part of the vessel, and are disposed of in various ways, to be described hereafter. The passage of vapours into the vessel is continued until a sample, drawn from a tap, shows that the acid is sufficiently saturated. It is best to leave a slight excess of acid, in which case the liquor,

after evaporation in leaden pans by indirect steam, yields whiter sulphate.

With more concentrated acid another form of saturator is used, consisting of a tank not completely closed, to which, as the acid becomes saturated, more strong acid is added, either from time to time or in a continuous thin jet. The waste gases and steam in this case are drawn away from the closed part of the tank by means of a chimney-draught, which must be strong enough not to allow any gas to escape out of the open portion; this can be still better secured by a fan-blast or an injector. As the solution becomes supersaturated with ammonium sulphate, this salt crystallizes out, in spite of the heat. In some cases this is continued till the liquor becomes too thick, whereupon the whole contents of the saturator are drawn out by means of a bottom tap into a cooler, from which,

Fig. 149.



after the crystallization is complete, the mother-liquor is pumped or ladled back again into the saturator. In other cases the salt is fished out from the saturator during the operation itself. This is done in a "fishing-box," represented in fig. 148. It consists of a wooden vessel lined with lead, and divided into two compartments by the lead curtain, *a*, which dips into the acid. The outer compartment is lower, and open at the top; the bottom is made to

slope to this side. The other compartment is closed by a lid, perforated for the tube, *b*, through which the ammoniacal vapours arrive, for the exit-pipe, *c*, and the acid-pipe, *d*. The sulphate precipitating during the operation is raked towards the open end, and fished out there from time to time by a perforated ladle. The best form is that in which the bottom of the open compartment is made into a well, in which fits a strainer; the salt drawn from the closed compartment falls into this strainer, which from time to time is lifted out to empty the salt. Fig. 149 shows this arrangement.

A saturator constructed on this principle, which has long been well known to practical men, and has been carried out at many works (it is also described and figured in my German work of 1867), has been patented by W. Arrol and J. Meikle (B. P. 12174, 1884). The only novelty their patent contains is that their vessels are not made of lead, but of copper—an invention not likely to be infringed by others.

Watson Smith (priv. comm.) recommends the following plan for obtaining perfectly white sulphate :—The saturator is charged with acid at 80° Twaddell, and ammonia is passed in until there is a slight smell of it. The excess is neutralized by a little acid ; and the separated sulphate is *at once* fished out, whereupon the operation can commence again. If, however, the acid is run in little by little, and the gas passed through for a long time, the separating sulphate is black ; and so it is in the former case, if, when the liquor has been proved by its smell to contain an excess of ammonia, fresh acid is run in and fresh gas is passed through, without fishing out the sulphate already formed, so that it is allowed to accumulate. In fact the rule is, to fish out the *freshly deposited* sulphate from *tolerably acid* mother-liquors. The fishing is done by means of a ladle of galvanized iron, perforated with numerous small holes; the sulphate is thrown upon a lead-lined drainer, from which the mother-liquor runs back into the saturators.

In the case of discontinuous saturators, it should not be forgotten that solutions of ammonium salts, when boiled, give off some free ammonia. Hence the acid, when nearly saturated with ammonia, hot as it is, will not completely retain it, especially if the bubbles of gas are rather large. For this reason the points of contact should be multiplied, and the gas-pipe should not dip to too small a depth in the acid. In the case of very large apparatus, it might

be best to employ two saturating-boxes in succession, the upper one to be charged with fresh acid; the gas would have to pass first through the lower box, where it would give up nearly all its ammonia, the rest being absorbed in the upper box. When the contents of the lower box have been run off, those of the upper box should be run down into it, and fresh acid charged into the upper saturator.

In England, usually, *sulphuric acid made from brimstone* is employed in the manufacture of sulphate of ammonia, because pyrites acid contains iron and arsenic, both of which discolour the sulphate. F. C. Hills (B. P. 3257, 1878) avoids this by allowing the pyrites acid to meet with an excess of ammonia, which precipitates iron and arsenic (?); the excess of ammonia is absorbed in another vessel, in the manner described in the patent. In Germany nothing but pyrites acid is used; the resulting sulphate has a grey tinge, but is as valuable for manure as the best white. Such grey sulphate is also very commonly found in England. The pyrites acid ought, however, to be made from pyrites containing very little arsenic; that made from Spanish pyrites (which is now practically the only one used in England, and is often employed in Germany as well) is objectionable because it contains too much arsenic, which produces yellow sulphate—a colour not at all liked by the consumers. Some German makers produce white sulphate, even from strongly arsenical acid, by skimming off the arsenic trisulphide from the top of the saturator, which, of course, necessitates an open form of this apparatus. W. A. Meadows (B. P. 5520, 1884) purposely adds a small quantity of tar, pitch, oil, fat, or the like, and carries on the operation at a temperature not below 38° C. In this case a scum is formed on the top, which contains the arsenic and iron of the sulphuric acid, and facilitates their removal. An American patent by E. A. Falls (No. 318,972) covers the same invention. A much better process, which the author saw at a Dutch factory, where it had been at work most successfully for a number of years, is the following:—Ordinary pyrites acid is used, of specific gravity 1·71. To this a certain quantity of "*vitriol-tar*" is added; that is, the sulphuric acid which has served for making crude benzol, and which is charged with a large quantity of tarry impurities (p. 444). On the acid being saturated by the ammonia coming over, the tarry matters are precipitated and rise to the surface, carrying along and enveloping the arsenious sulphide formed at the same

time from the pyrites acid. The scum is carefully removed, and the sulphate fished out after this is perfectly white, as I could see from the large quantity kept in stock. Thus the "vitriol-tar," which formerly was an intolerable nuisance, is utilized not merely for its acid, but even its tarry impurities are made to serve a very useful purpose. A similar, but much more complicated patent process has been described, p. 445.

The prejudice against pyrites acid seems to be likewise going out in England. At least at one of the very largest ammonia-works the author was told that they used it as well as brimstone acid; the sulphate made from the former was somewhat discoloured, but fetched exactly the same price as the white sulphate made from brimstone acid.

Sulphuric acid in the form of a spray is employed for absorbing ammonia by Neumayer and by Wellstein; comp. p. 564.

Sulphurous acid has been employed for this purpose, with the idea of converting the sulphite into sulphate by the action of air, partially or entirely, by Laming, in 1852; by G. E. Davis*; by Addie, for absorbing ammonia directly from blast-furnace gases (p. 558); by Young (comp. later on); by A. McDougall (B. P. 15496, 1884), who passes kiln-gases from sulphur- or pyrites-burners into an ordinary saturator, and oxidizes the crystallizing ammonium sulphite to sulphate [so far there is nothing new in the patent], whilst the mother-liquor, containing sulphite as well, is used for scrubbing coal-gas, in which case it absorbs ammonia and decomposes the hydrogen sulphide with precipitation of sulphur.

Kieserite (*native magnesium sulphate*), from Stassfurt, is employed by Kelly and Weigel (B. P. 8680, 1884) in this way:—A mixed solution of kieserite and common salt is cooled down, whereupon sodium sulphate crystallizes out. This is treated by ammonia and carbonic acid; the resulting sodium bicarbonate is separated by filtration, and from the mother-liquor ammonium sulphate is recovered. This is evidently more a process belonging to the domain of alkali-making. This is also the case with Gerlach's process †, which is founded upon decomposing concentrated gas-liquor by sodium chloride, sulphate, or nitrate, and passing a stream of carbon dioxide into the liquor, whereupon sodium bicarbonate is precipitated, and ammonium chloride, sulphate, or nitrate

* Journ. Soc. Chem. Ind. 1883, p. 521.

† Dingler's Journal, vol. ccxxiii. p. 82.

remains in solution. This process has never been practically carried out.

The *residue from distilling ammoniacal liquor with lime* is nearly always thrown away, and is sometimes a source of trouble on account of nuisance, as we shall see further on. But it has been proposed to utilize it for recovering from it whatever *ferrocyanide* the gas-liquor contains, by neutralizing it with acid, when Prussian blue will be precipitated (H. Bower, B. P. 2918, 1882). The same inventor prescribes converting the cyanide in raw gas-liquor into ferrocyanide previous to distilling it with lime—a somewhat unnecessary precaution, as the very small proportion of cyanide originally present seems to find enough iron, in all practical cases, in the vessels &c. to be converted into ferrocyanide. Its quantity is, however, so small that it will hardly pay recovering.

There is, however, *much more ferrocyanide in the spent oxide.* This is not easily recovered by dissolving the Prussian blue in caustic alkali, as too much alkali is required and much sulphur is dissolved at the same time. Hempel and Sternberg (G. P. 33926) treat the spent oxide, after having first removed the ammonium salts by washing, with liquor ammoniæ of 10–12 per cent. This dissolves the Prussian blue as ammonium ferrocyanide, without acting on the sulphur. From the solution the Prussian blue can be precipitated by acid, or else it is distilled with lime to recover the ammonia, and the calcium ferrocyanide is converted by potassium carbonate into potassium ferrocyanide.

Kunheim and Zimmermann (G. P. 26884) desulphurize the spent oxide as usual, remove the ammonia salts by lixiviation, dry the residue in the air, mix it with dry caustic lime in powder, and heat to 40°–100° to expel the "insoluble ammonia." The product by extraction with water yields an ammoniacal solution of calcium ferrocyanide. This is carefully neutralized and heated to boiling, when an insoluble double ferrocyanide of calcium and ammonium is precipitated. The further working-up into Prussian blue or into potassium ferrocyanide is described in the patent (abstracted in Dingler's Journal, cclii. p. 478, and Journ. Soc. Chem. Ind. 1885, p. 112).

The *concentrating-pans* for ammonium sulphate are generally made of lead and heated by leaden steam-coils, because iron would be acted upon during the escape of free ammonia. According to P. S. Brown (B. P. 804, 1878), iron pans may be used if care is taken to keep the liquor always slightly alkaline.

Prevention of Nuisance; Treatment of the Waste Liquors and of the Gases escaping in the Saturating-process.

Sulphate-of-ammonia works are, if badly conducted, a great nuisance to the neighbourhood, principally in consequence of the offensive gases given off in the saturation-process. The gases escaping consist of carbon dioxide, sulphuretted hydrogen, sometimes a little hydrocyanic acid, a small but very perceptible quantity of hydrocarbons, and perhaps also of sulphuretted organic compounds; all of them mixed with a large amount of steam.

If this gaseous mixture were allowed to escape freely into the atmosphere, the nuisance would be altogether intolerable. It is bad enough if only a small proportion of it finds its way outside the works; even then the nuisance may be perceived at a distance of half a mile or more. Nor can the offenders easily escape detection; the smell of these gases is easily recognizable by its peculiarity. The public have a special dread of it, and thus any escape of this kind is sure to be soon traced to its origin and is fruitful of complaints.

Dr. Ballard (Report of the Medical Officer to the Local Government Board for 1878, p. 131) expresses himself as follows about this matter:—"Medical men are usually ready to certify that the effluvia are injurious to public health, probably referring the effects produced on those who are exposed to their influence in a diluted form, to the operation of the sulphuretted hydrogen as a poison. The public also readily believe that an atmosphere even slightly thus contaminated is dangerous to live in. It is certain that exposure to the diluted effluvia from sulphate-of-ammonia works does in many persons induce feelings of depression, headache, loss of appetite, nausea or vomiting, and sometimes some oppression of the breathing."

The following are the principal sources of nuisance from such works:—

1. The *reception, transference, or storage of the ammoniacal liquor*.—This can be made innocuous wherever the sulphate-works are within reasonable distance of the gas-works, which produce the ammoniacal liquor, by conveying it by means of pipes. Dr. Ballard recommends underground pipes; but we should decidedly prefer overground pipes, wherever possible, as in the former kind leakages may occur and continue for a long time without being

detected. Wherever the liquor has to be conveyed to a greater distance, tank-waggons or barges are employed, exactly similar to those used for conveying gas-tar, and similar precautions should be taken in both cases. Pipes should be laid from the gas-works to the place of loading; the tank or hold of the boat should not be covered with loose planks in the perfunctory way often noticeable, but closely; the tar or liquor should be introduced by a close conduit, and, to prevent all nuisance, provision should be made for the escape of air from the tank through a box containing trays charged with hydrated iron peroxide. Tank-waggons should be charged from elevated reservoirs by a hose, through a man-hole at the top, without exposure to the air; the man-hole is afterwards closed by a tightly screwed-down lid. On arriving at the sulphate-of-ammonia works, the liquor should be run or pumped into the reservoirs with similar precautions, the vent through which the air must escape being guarded by a small oxide-of-iron purifier.

2. *Leakages about the apparatus* may cause local escapes of foul gases. This may occur about the angles or edges of the curtain in fishing-boxes, by lids not being properly fastened down, by insufficiently luting the curtain with liquor, and the like. Nuisance arising from such cases must be instantaneously detected by those in charge of the works, and can be prevented by ordinary care.

3. *The waste liquor and lime from the stills* may likewise cause nuisance. Usually these waste liquors are discharged while hot, and the slight proportion of ammonia they contain is then given off, and causes a very perceptible smell in the neighbourhood. The obvious remedy is, to thoroughly exhaust the liquors. Dr. Ballard mentions that Mr. Steuart, of Clayton, reduces the ammonia in the liquor down to 0·002 per cent. The hot waste from the still should not be conveyed away by an open channel, but by a pipe. Before reaching a common sewer or public watercourse, it must necessarily pass through a settling-tank, both in order to separate the solid refuse from the liquor, and to completely cool the latter before it gets into any sewer with which house-drains communicate, or into any watercourse in which fish exist. The settling-tank should be covered over, and should be ventilated merely by a pipe of sufficient length to condense any vapours rising through it. The lime-deposit (which contains a great deal of calcium sulphide) should never on any account get into the

sewers or watercourses, where it is sure to give off sulphuretted hydrogen. Even when it is entirely kept back in the settling-tank, it may cause nuisance when being disturbed for removal, and again when depositing it on a heap. It should therefore be removed as expeditiously as possible, and with all possible precautions against unnecessary exposure to the air. It should be covered up during transmission from the premises, and if shot down in any open place where it is likely to be a nuisance, the surface of the heap should at once be covered with earth and patted down. Wherever that is not possible, it is best to excavate large pits in the ground, which, after being nearly filled with waste lime, are covered up with soil again. But in this case care must be taken that no nuisance arises by foul drainage from such pits.

In some cases such lime-deposit may be utilized by grinding it up with a little fresh lime and a good deal of cinders or the like, when it will form a very well-setting and somewhat hydraulic mortar, which approaches in composition the well-known Scott's cement.

Even when the waste liquors have been completely clarified by repose, and have been practically freed from ammonia, the neighbours or the public authorities often oppose their discharge into public watercourses, on account of the tarry matters, which give them a brown colour and a certain smell. Such opposition is even sometimes founded on quite unreasonable grounds, as the presence of calcium chloride, which, of course, is equally unavoidable and harmless; but the same cannot be said of the tarry matters &c. Sometimes, owing to the presence of such matters, the liquors will not even readily clarify. In such cases a remedy, as I have convinced myself by experiment, is nearly always possible by producing in the liquor a precipitate of hydrated oxide of alumina or iron, which carries down the tarry matters and other impurities, and leaves a nearly colourless and quite inoffensive liquid. Such a precipitate is caused by adding a sufficient quantity of sulphate of alumina, or, preferably, of sulphate or chloride of iron, along with sufficient lime to completely precipitate the metallic base, but no more.

Since the removal of objections from this cause may be a matter of life or death to ammonia-works in some localities, we will here give a detailed description of a *mechanical arrangement for purifying refuse liquors*, which has been in successful operation at

the workmen's colonies at the immense steel works of Krupp, near Essen, for a long time past, and which can therefore be safely recommended. I owe the following description and diagrams to the kindness of Dr. Salomon, chemist at the above works. It should be noted that the plant is there applied to the purification of ordinary sewage, but that nearly every thing applies just as well to waste liquors from ammonia works (as also to those from dye-works and a very great many other sources).

The purifying process is based upon the fact that all the substances mechanically suspended in the water, as well as a large portion of those kept in solution, but in any case those which are easily decomposed [this, of course, applies to sewage], are precipitated and decomposed by a proportionately small addition of lime and sulphate of iron (copperas). It is indispensable that the lime, as principal agent, should do its work alone at first, and only after it has fully exerted its decomposing action must the ferrous sulphate be added [this, of course, only applies to sewage].

The clarifying plant is shown in the annexed figures, 150 to 152, giving a ground-plan, a longitudinal and a cross section. It consists of the following parts:—The catchpool, A; the feeding-apparatus for chemicals, B; the settling-tanks, C C, for the liquid saturated with lime; the tanks, D D, for precipitating with ferrous sulphate; the catchpools, E E, for retaining any flocculent precipitate still suspended in the liquid; the waste-channel, F; the mud-tank, G; the clear-water reservoir, H.

The liquid first runs into the catchpool A, where the heavier substances suspended in the water and those floating on the top are retained. From there it flows into one or other of the feeding-vessels, B B; two of these are provided, so that one may be always in operation. They contain a small overshot waterwheel, the prolonged axle of which carries on either side a cross with baling-buckets and a stirrer for each of the tanks, separately holding milk of lime and solution of copperas. This water-wheel is turned by the inflowing waste liquor itself, and will, of course, turn more or less quickly according to the supply of such liquor; hence the baling-buckets, fixed at the sides of the wheels, will take up more or less of the chemicals, exactly in accordance with the quantity of liquor to be purified. Thus the supply of chemicals is self-regulating, and only requires the filling up of the reservoirs from time to time with milk of lime and solution of copperas. The

number and size of the baling-buckets must be determined once for all by practical trials, as well as the concentration of the chemicals. The milk of lime taken up by the buckets fixed to one side of the wheel is discharged into the waste liquor just below the wheel; but the copperas solution taken up by the buckets on the other side of the wheel is conveyed in a special conduit into the reservoirs, D D. The liquor, mixed with a sufficient quantity of lime, flows by a channel into one or other of the tanks C C (there are two of these, so that one can be cleaned out without interrupting the work of the other). It runs on in the direction of the arrows, and the

Fig. 150.

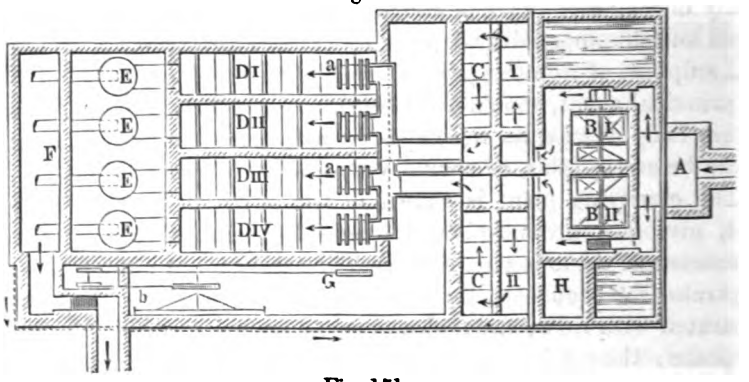
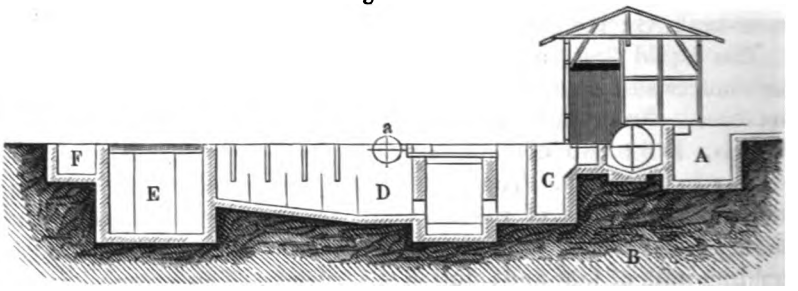


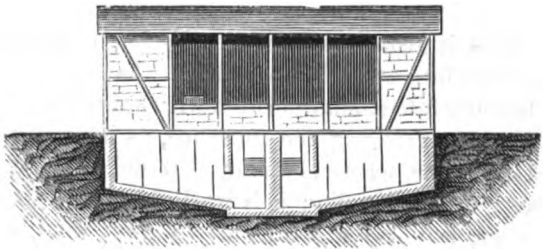
Fig. 151.



zigzag partitions arranged in the tanks cause a large portion of the suspended matters, along with those precipitated by the lime, to settle down. The liquor, still saturated with lime, is run by means of a spreading-shoot into one of the four separate tanks, DI, DII, DIII, or DIV, where it meets with the copperas solution coming from BI or BII. This causes a thick, flocculent, dark green precipitate to be formed, consisting of ferrous hydrate and calcium

sulphate, which quickly settles down as the liquor travels on, and carries down all the finely divided matter still in suspension. [I have proved by experiment that nearly all the tarry matters found in waste ammonia liquors are carried down here, and the liquor issues nearly, or even quite, devoid of colour and smell.] The flow is here also broken by zigzag partitions and checks; but in order to better retain the flocculent precipitate there are also peat-filters placed in the way of the liquor, in lieu of ordinary checks. A small agitator, *a*, causes an intimate mixture of the liquor and of the copperas solution. The necessary moving-power may be either derived directly from the wheels in B B, or else from a separate wheel driven by the clarified water; but the latter is only possible where there is a sufficient head of water at disposal.

Fig. 152.



Since, in order to completely retain all the flocculent precipitate, the tanks D D would have to be made of an inconvenient length, another arrangement is provided for that purpose. This is the set of catchpools E, E, E, E, from which the completely clarified liquor runs away through F.

In some cases [especially with sewage] it will be necessary to restore to the outflowing liquid the oxygen taken away from it by the ferrous hydroxide. If the outflowing liquor is used for driving a water-wheel, as is shown in fig. 150 at *b*, there will be sufficient contact with atmospheric oxygen as the liquor is running over the wheel. In other cases such contact can be caused by special means (probably unnecessary in our case).

The mud collecting in the tanks C C and D D is from time to time removed by taking out the checks and opening the discharge-valves. It then flows, with sufficient fall, into the mud-tank G, and is pumped up from here by a dredger or other suitable means,

in order to drain in special filtering-basins. It is possible to keep the lime precipitated in C and the iron precipitated in D separate, and to utilize the former for agricultural purposes.

The milk of lime and the copperas solution ought not to be made with foul liquor, but with clear water. For this purpose that coming from F may be conveyed into the tank H, and can be pumped up from here as it is required.

The plant shown here serves for daily purifying from 2000 to 3000 cubic metres (say, tons) of concentrated sewage; it costs about £750, inclusive of mud-filters, and requires only one man for superintendence, as everything is self-regulating.

4. *Treatment of the offensive Gases and Vapours liberated in the Saturator.*—These gases and vapours are the most ordinary source of complaints of nuisance, and from this cause (as well as from the preceding one) legal proceedings have been several times taken.

In some cases it seems sufficient to discharge these gases &c. from the separator into a tall chimney-shaft. Especially where they can be first brought into communication with hot furnace-gases, this seems to suffice for removing the nuisance, as is proved by some works in Manchester, where shafts of 180 and 195 feet serve for this purpose. Where the liquor is worked up at the gas-works themselves, there is never any difficulty of that kind, as the immense volume of highly-heated gases coming from the retort-fires is far more than sufficient to burn and dilute all effluvia from the ammonia-plant. But in other cases, where there is no very tall chimney-shaft, or even with a tall shaft but an unfavourable conformation of the country, a thorough combustion of the gases must be aimed at. This is ordinarily done by carrying them by a pipe from the saturator into the side of the boiler-fire, or under the fire-grate, or sometimes into a fire specially kept up for this purpose. But unless care is taken to remove the large quantity of watery vapour contained in the gases, the object in view will be imperfectly performed, or even quite frustrated by the vapours extinguishing the fire. It should therefore never be neglected to provide means for condensation. At some works the pipe which conveys the gases is continued into a worm, passing through a tank filled with gas-liquor or with water for feeding the steam-boilers, which are thus heated up previous to use. At the Plymouth gas-works an 8-inch pipe from the saturator is first carried

beneath the floor on which the sulphate is dried, and thence runs along the surface of the ground, where it is bent upon itself, for a distance of about 500 feet, in the course of 290 feet of which it is played upon by jets of water flowing from a perforated pipe above it. At the Stampshaw works the 8-inch pipe from the saturator is first carried round the outside of the building at the eaves, and then enters a worm-condenser. At Illingworth's works at Bradford special care is taken to remove the watery and any other condensable vapour, as the sulphuretted hydrogen is there utilized for the manufacture of sulphuric acid. The gases are first conducted into a chamber, made of an old boiler, through which the pipe conveying the liquor to the Coffey still passes, and they thus serve to warm the liquor; then by a pipe to two iron towers, divided by partitions springing at opposite sides alternately in such a way as to make a tortuous passage for the vapour; and, lastly, from these towers through a long series of vertical iron pipes, bent upon themselves in the manner of a continuous condenser, such as is used in gas-works, water being made to flow continually down the outside of the pipes from a perforated water-pipe above. Other means for cooling the gases, and condensing the watery vapour therefrom, will be mentioned when describing in detail some of the varieties of plant observed by myself.

The condensed liquid, if not quite cold, may by itself cause a nuisance, and should therefore be cooled down before discharging it into a public drain.

The *combustion of the dried gases* is usually carried out by making them pass through a small coke-fire; and the sulphurous acid produced by the combustion of the sulphuretted hydrogen is usually discharged with the fire-gases up the chimney, and thus thrown away. Sometimes the gases are burned by themselves, *e. g.* at Messrs. Forbes and Abbott's works at Old Ford, where they enter by a 1-foot square opening into a small fire-brick chamber and thence into a fire-brick flue, about 15 feet long, 2 feet 6 inches wide, and 3 feet high; air is supplied by a small circular hole in an iron plate near the entrance of the gas, and the gases are ignited. Once the chamber and flue are red-hot, there is no fear of the gas being accidentally extinguished without re-lighting. The heat thus generated is then utilized for heating steam-boilers, which are said to have lasted for 14 years without receiving any injury by corrosion from the acid gases. The pro-

ducts of combustion, containing a large proportion of sulphur dioxide, are sent up the chimney-shaft.

Chateau* describes the apparatus used at Arcueil for deodorizing the gases evolved in the manufacture of sulphate of ammonia. They are aspirated by a fan-blast through a coke-column, 17 feet high, in which is spread a mixture of ferric oxide and calcium sulphate, constantly moistened by a solution of ferrous sulphate. Here ammonia and carbonic acid are retained [?]. The gases on issuing from the fan-blast pass over a thin layer of camphor and then into a combustion-furnace constructed by M. Perret. The grate-bars of this furnace are only $\frac{1}{24}$ inch apart, and are so deep that they can be made to dip into a water-basin in order to cool them and retain their shape. The gas enters in the narrow space between the water-basin and the grate. The latter is charged with anthracite dust, which is partly carried away by the gaseous current, but is completely burnt in zigzag flues, made of fireclay flags, which soon attain a white heat. At this high temperature hydrogen sulphide, ammonium sulphide, cyanogen compounds, and any other deleterious gases are completely burned, air being admitted by special openings for this purpose. The strong heat generated is employed for firing a steam-boiler. The apparatus is in regular operation, and is said to give very satisfactory results.

It should not be forgotten that the sulphurous acid discharged from a chimney may itself cause a nuisance—no doubt much inferior to that which the sulphuretted hydrogen would have produced, but still sufficient to give rise to complaints. Besides this it may sometimes happen that the sulphuretted hydrogen is but imperfectly burned, and that enough of it escapes to create a nuisance.

All this can be overcome by one of two ways—either absorbing the sulphuretted hydrogen by some means, or burning it and *utilizing the* SO_2 *to form sulphuric acid.* The latter process has been in practical operation for several years past, first at Mr. Illingworth's works at Frizinghall, near Bradford, then at Messrs. Spence's works at Birmingham, and probably elsewhere. The gas is burned in a fire-brick chamber, 12 feet long, 3 feet deep, and 4½ feet wide, into which at one end the gas (previously carefully dried) is admitted by a pipe. There is a small air-opening

* Bull. Soc. Chim. xxxvi. p. 195.

close by. The products of combustion must pass through several pigeon-holed walls built across the chamber, in order to mix the gases and make the combustion perfect. They then play round the usual nitre-pots, and the mixture of SO_2, steam, nitrous fumes, nitrogen, CO_2, surplus air, &c. is carried into ordinary vitriol-chambers. If the combustion-chamber is once properly heated, the gas keeps lighted and the combustion proceeds satisfactorily; but when the work is not going on, for instance on Sundays, the heat of the chamber is maintained by a small coke-fire, burning on a grate just below the entrance of the gas-pipe.

It cannot be doubted that this process is entirely successful in removing all nuisance; but the presence of carbonic acid &c. in the gases is very injurious to the acid-forming process, and it seems doubtful whether there is, under ordinary circumstances, much profit to be made out of it*. But it must be said to have answered its purpose if it effects the removal of the nuisance from the waste gases, even without any profit accruing from the process.

There is no reason why Schaffner and Helbig's process for *manufacturing sulphur by the partial combustion of sulphuretted hydrogen* should not be applied in this case. This process, which is described in detail and explained by diagrams in my 'Manufacture of Sulphuric Acid and Alkali,' vol. ii. p. 689 *et seq.*, consists in burning one third of the gas and decomposing the SO_2 thus formed with the remaining H_2S into water and sulphur, in the presence of a solution of calcium chloride, which causes the precipitate to assume a manageable form. The reaction taking place is

$$SO_2 + 2H_2S = 2H_2O + 3S.$$

The presence of carbonic acid &c. in this case does not do any harm, and the product is much more valuable than sulphuric acid. It does not, however, seem that this process has as yet been carried out in sulphate-of-ammonia works.

One of the most direct methods for dealing with sulphuretted hydrogen is the process patented by C. F. Claus (B. P. 3606, 1882), which is said to be successfully at work at several ammonia-works. The gas is mixed with a carefully regulated quantity of

* An inquiry made to one of the firms named in the text, dated August 1886, has not elicited any reply.

air, containing about sufficient oxygen for burning the hydrogen of the H_2S, and the mixture is passed through a chamber in which it has to traverse a hot layer of porous material, such as oxide of iron, oxide of manganese, &c. Here the hydrogen of the sulphuretted hydrogen is burned into water, and sulphur is set free, the heat of the reaction keeping up the temperature of the contact-substance without any external heating being necessary. The steam and sulphur vapours pass on into a series of chambers where they are condensed by air-cooling, and from which the sulphur is from time to time removed. At last the gases may be passed through a tower filled with coke or with pieces of limestone, water flowing down the same, in order to absorb any sulphur dioxide formed in the reaction.

The same inventor has taken out additional patents (Nos. 5070 and 5959, 1883), in which he describes various descriptions of porous material, *e. g.* oxide of iron mixed with lime, alumina, magnesia, and the like (because pure oxide of iron sometimes develops too much heat), formed into a pasty mass, which is dried and broken to pieces; or oxide of copper, oxide of manganese, or other "pyrophoric" or contact-substances which will decompose hydrogen sulphide at the ordinary temperature. In the case of soluble substances, as sulphates of copper, iron, zinc, &c., they are dissolved in water, and pieces of burnt porous clay, asbestos, pumice, &c. are soaked with this solution and dried. All these substances are used in pieces not larger than a walnut nor smaller than a pea, in layers of from 6 to 12 inches thick on the perforated false bottom of a closed iron tank lined with brick. This answers best for gases containing from 15 to 25 per cent. H_2S; for poorer gas, layers of a thickness of 6 feet or upwards may be employed, but 6 inches may be considered the minimum thickness even for the richest gas. In this way the sulphur may be recovered from gas mixtures containing only 3 to 5 per cent. of H_2S.

When the porous contact substance is composed of hydrated oxide of iron or manganese, it need not be heated up before commencing to pass into the kiln the mixture of gases containing H_2S and free O. Such hydrated oxides start the reaction at ordinary temperatures; and though the heat developed by that reaction soon renders them anhydrous, or nearly so, it at the same time raises the porous bed to such a temperature that it can henceforth

maintain the reaction. The patent also includes the possibility of heating, in case of necessity, the porous bed by heat from some other source. At Hull, where the process is employed in connection with the manufacture of ammonium sulphate, it gave 3·70 grains of SO_3 per cubic foot as the highest, and 0·3 grain as the lowest quantity left in the gases after being treated in the above way (communicated by Mr. J. G. Holmes). At Birmingham a 15-inch layer of oxide of iron, heated to redness in a kiln, is employed, as described by C. Hunt*, who also mentions the apparatus constructed by Claus for obtaining a rich gas-liquor from ordinary scrubber-liquor as a continuous process in purifying coal-gas.

C. W. Watts, who also describes the Claus process for purifying coal-gas †, gives the following more detailed description of the apparatus for burning the H_2S. This is done in a "kiln," that is, a small chamber built of fire-brick and enclosed in a shell of cast-iron plates. In that special case it is a circular chamber, 2 ft. 6 in. in diameter and 3 ft. high; it contains a layer, 15 in. deep, of oxide of iron in lumps about 1 in. in diameter, supported on a grating built of 1 in. split fire-bricks set on edge. A space of about 1 foot above the oxide is empty, and the gas enters this space, passes downwards through the oxide, and out from below the grating into the depositing chamber. This is a brick building, 24 ft. long by 8 ft. wide, and 5½ ft. high, with 9-in. walls, and flat roof of ¾-in. slates. Transverse baffle-walls are built inside the chamber, which open alternately on one side and the other of the chamber, so that the gases are forced to traverse the whole area of the chamber before reaching the outlet. Previous to entering the kiln the gases are mixed with a quantity of air (supplied by a small air-pump) 2½ times the volume of the sulphuretted hydrogen. At starting, the kiln is filled with hydrated oxide of iron (manganese or other metal); the ordinary reactions take place between the substances present, sulphide of iron being formed, and immediately reoxidized by the air, and, as these reactions take place in a small confined space, the heat accumulates until the whole mass is red-hot. At this temperature, of course, the sulphur produced by the reaction is immediately volatilized, and passes with the other gases into the depositing chamber, where

* Journ. Soc. Chem. Ind. 1886, p. 445.

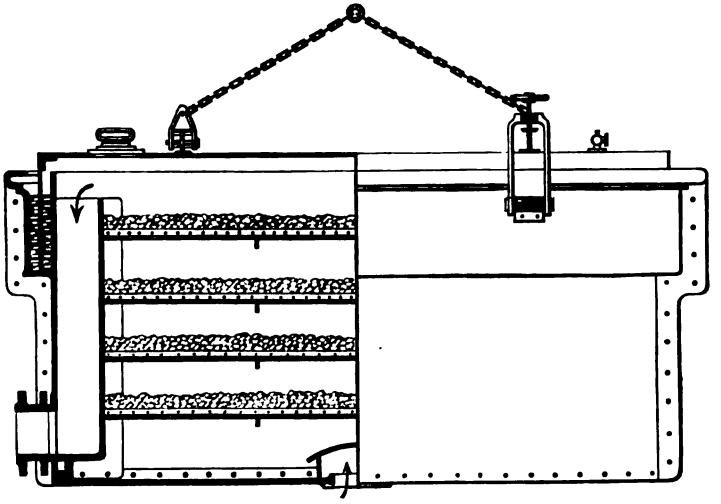
† Ibid. 1887, p. 25.

it settles. As the proportion of sulphuretted hydrogen in the gas is not quite constant, it generally happens that there is either a slight excess or a slight deficiency of air supplied. There will then be a small quantity of either sulphuretted hydrogen or sulphurous acid at the outlet. To prevent the escape of these gases into the air, a wash-tower filled with pebbles and supplied with a little water is connected with the chamber, and beyond this is a small open oxide-purifier. The water absorbs any SO_2 that may be present, and the oxide of iron any traces of H_2S. The sulphur obtained amounts to about 90 per cent. of the theoretical quantity. It is very pure, containing over 99 per cent. of pure S, after deducting the moisture that is generally present. The gases from the liquor contain small quantities of naphthalene and other hydrocarbons, and these being charred in passing through the kiln, impart a brownish tinge to the sulphur. The amount of carbon present, however, does not amount to 0·1 per cent.

Instead of burning the sulphuretted hydrogen, it is sometimes, especially at smaller works, *absorbed in a purifier, charged with lime or oxide of iron.* For this purpose the condensable vapours must be equally removed by cooling; and the dried gases are then passed into purifying-apparatus, constructed exactly like those used at the gas-works, and for the same purpose, as shown in fig. 153. They are cast-iron boxes, provided with a rim at the top for an hydraulic lute, into which dips the flange of the cover. The gases enter at the bottom and pass through trays, usually made of wood, on which the purifying-material is spread out in a layer of 3 or 4 inches. The purified gas finds its way out through a pipe from the upper portion of the box. Several such boxes are usually combined, so that they can be worked in regular rotation, that box receiving the fresh gases which has been the longest time at work, and that receiving the gases just before escaping into the atmosphere which has been last charged with fresh material. Such boxes are made, for example, from 10 to 20 feet square and from 2 to 4 feet high; they may also be made of brickwork, but they should not be made of wood, as it is difficult to keep them tight in that case. Moreover the heat developed in the absorption of H_2S may injure the wood, and for this reason it is also preferable to substitute perforated iron or wire-gauze trays for those made of wood.

Sometimes the absorbing-material used is lime; but this is anything but rational. The lime is wasted once for all, and the spent lime ("blue-billy") is a fresh nuisance, which may cause considerable trouble. A much better material is that used at nearly all gas-works, namely the hydrated peroxide of iron,

Fig. 153.



generally mixed with saw-dust; or else the similar material patented by Mr. Friedrich Lux, of Ludwigshafen. This material, when it has ceased to be active, can be regenerated by simple exposure to the air, which causes the iron sulphide to be converted into a mixture of ferric hydrate and free sulphur; and when the sulphur has accumulated to such an extent that the material becomes definitively useless for absorbing H_2S, the "spent oxide of iron" is a valuable material for the production of sulphuric acid, so that its sulphur is turned to a useful purpose.

Sometimes a fan-blast or an injector of some kind is used for driving the gases through the purifiers.

We will finally quote the process of Young (B. P. 1310, 1880), who conveys the ammoniacal vapours, evolved without using lime, not through a saturator, but along with air through a fireplace, where the ammonium sulphide is partly burned into sulphite and partly into sulphate, which are conveyed into a suitable condenser. The ammonium sulphite is converted into sulphate by passing a

current of heated air through the solution (as previously proposed by Laming). Since the gas-liquor never contains enough sulphides to convert all the ammonia into sulphate, sulphur dioxide is mixed with the products of distillation before or after they have passed through the fire, or else the condensed liquid is saturated with sulphurous or sulphuric acid. This process is evidently altogether analogous to that patented by Messrs. Addie for blast-furnace gases; it suffers from the difficulty that at the high temperature employed a good deal of ammonia will be burned, and that the condensation of the highly heated ammonia compounds diluted with air is not an easy matter; comp. also p. 558.

The last-mentioned process already belongs to those which aim at preventing the formation of H_2S before the gases enter the saturator. The same object is followed by those who add to the liquor, *before distillation*, substances calculated to retain the sulphides, such as lime, hydrated oxide of iron, or other compounds of iron or manganese. But these processes are much too dear and too troublesome to be applied to the manufacture of sulphate of ammonia, and they can only be discussed for the manufacture of liquor ammoniæ, under which they will be dealt with further on.

5. *The smell arising from the evaporation of the sulphate liquors*, where strong acid is not used, has been mentioned before. This smell has been likened to the odour from ill-kept pig-sties, and sometimes this vapour may be a nuisance at a distance of 200 yards or more—nearly as much as the saturator-gases. To obviate it, steam should be driven through the saturator for 20 minutes or half an hour before running off the finished solution into the evaporating-pans; and this steam should be carried off and condensed in the usual way (Dr. Ballard, *loc. cit.* p. 135).

Description of special Apparatus for the Manufacture of Sulphate of Ammonia or Concentrated Gas-liquor.

The number of apparatus proposed, or even actually employed, for working gas-liquor or other ammoniacal liquors is very great indeed; a complete enumeration of them would not be a useful task, and is not even to be attempted in this treatise. A great many of them are more or less unsuitable or quite obsolete.

I shall therefore only describe such of the older and more modern apparatus as I have myself, or thoroughly trustworthy informants, actually seen at work within the last few years, and shall append a short description of other apparatus patented quite recently. This refers also to the apparatus for manufacturing liquor ammoniæ, to be described hereafter.

Most of the apparatus mentioned below serve only for the production of sulphate of ammonia, but some of them serve equally well for preparing from gas-liquor &c. a concentrated crude solution of ammonium carbonate and sulphide, for the use of ammonia-soda works or any other purpose, in order to save the comparatively excessive carriage on the ordinary dilute gas-liquor. Some of them are also intended for making liquor ammoniæ, but this is best done by special apparatus.

I shall not detain myself with describing the simple boilers formerly in use, sometimes along with a sort of imperfect dephlegmating apparatus, but shall at once proceed to the description of apparatus more calculated to save fuel and labour. I begin with more simple apparatus; after these I shall describe the more perfect continuously working stills, which seem likely to be extensively used in the future.

Apparatus used in London.

Fig. 154 gives a sketch of the apparatus employed at a London works, where 100,000 gallons of gas-liquor are worked up per day, representing the product of 600,000 tons of coal per annum. The liquor arrives in canal-boats A, and is pumped up by the pump *a* into a large settling-tank B, where it remains for 24 hours. It is then pumped by the donkey-pump *b* into a "Coffey" still C, 30 feet high, 12 feet long, and 5 feet wide, into which steam of 2 atmospheric pressures is blown by 5 tubes. Here the volatile ammonium compounds are separated from the water and the non-volatile salts, which are usually run away into the canal because they only contain 3·5 per cent. of the NH_3, and do not pay for working off with lime. (This is a contention frequently made, but probably quite erroneous.)

The volatile ammonium compounds pass out of the top of the still through a 2½-inch worm, perforated with numerous ½-inch holes, into the cylindrical saturator D, made of strong lead (20 lb. per superficial foot), the lower two thirds being strengthened by

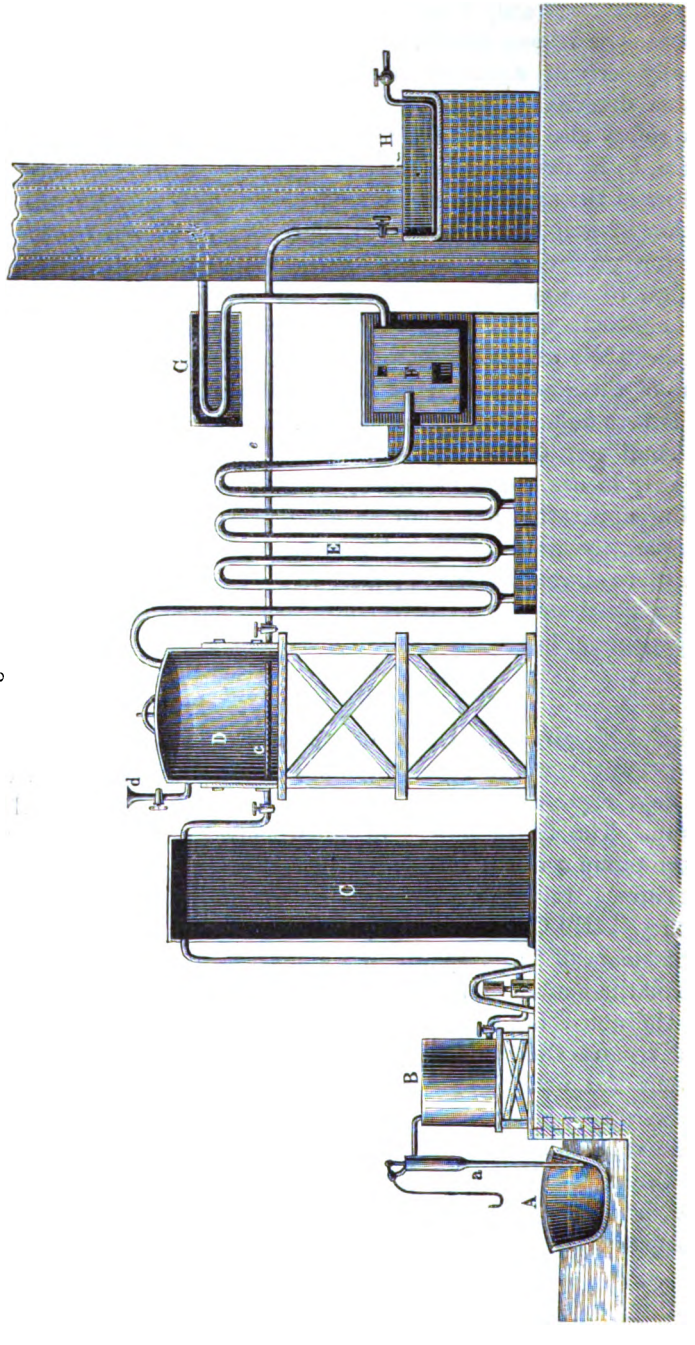


Fig. 154.

strong planks bound with iron hoops. It is 6 feet high and 10 feet wide, and is filled two thirds of its height, by means of the funnel-tap *d*, with a mixture of equal parts of brimstone acid of 140° Tw. and water, which remains in the apparatus till it is completely saturated. The acid is purposely diluted, to prevent the salt from crystallizing within the saturator. When the saturation is completed, the liquor showing only a very faint acid reaction, steam is blown through for a quarter of an hour, to drive off all the sulphuretted hydrogen. The vapours evolved in this process and during the whole operation pass first through the air-condenser E, to condense the moisture which is carried along, and then through a 7-inch metal pipe into the burner F. This is a square brickwork chamber, about 5 feet wide, 8 feet long, and 4 feet high, loosely packed with fire-bricks, which are made red-hot before the commencement of the operation. Here the hydrogen sulphide takes fire, and is kept burning afterwards by its own heat. The hot gases pass through a steam-boiler (indicated at G), where their heat is partly utilized, and thence into a chimney, in which no smell at all of hydrogen sulphide can be perceived [but what becomes of the sulphur dioxide formed ?]. The solution of salt is run from D through the pipe *e* into the lead pans H, 8 feet in diameter, 2 feet deep, made of 20 lb. leads heated by a steam-coil working at two atmospheric pressures. There is no smell perceived here. The ammonium sulphate crystallizing is fished out with a wooden spade, washed a little, and drained on a wooden floor. The mother-liquor serves for diluting the acid in the saturator. This process (*i. e.* saturating with dilute acid and evaporating the solution) is preferred to the continuous running-in of acid and fishing-out of salts, because the result is superior. This perfectly agrees with the statement (p. 602) quoted from Watson Smith.

Coffey's still was originally constructed for rectifying spirit of wine, but has been employed for many similar purposes, for ammonia first by Newton, in 1841. Fig. 155 represents the shape employed for spirit of wine: that employed for ammonia is essentially the same; but wood lined with lead is substituted for copper. It consists of an oblong vessel B and two superposed columns CDEF and GHIK. The former is called the analyzer, the latter the rectifier. The whole is made of 6-inch wood lined with lead, so that little heat is lost by radiation. B is divided into two

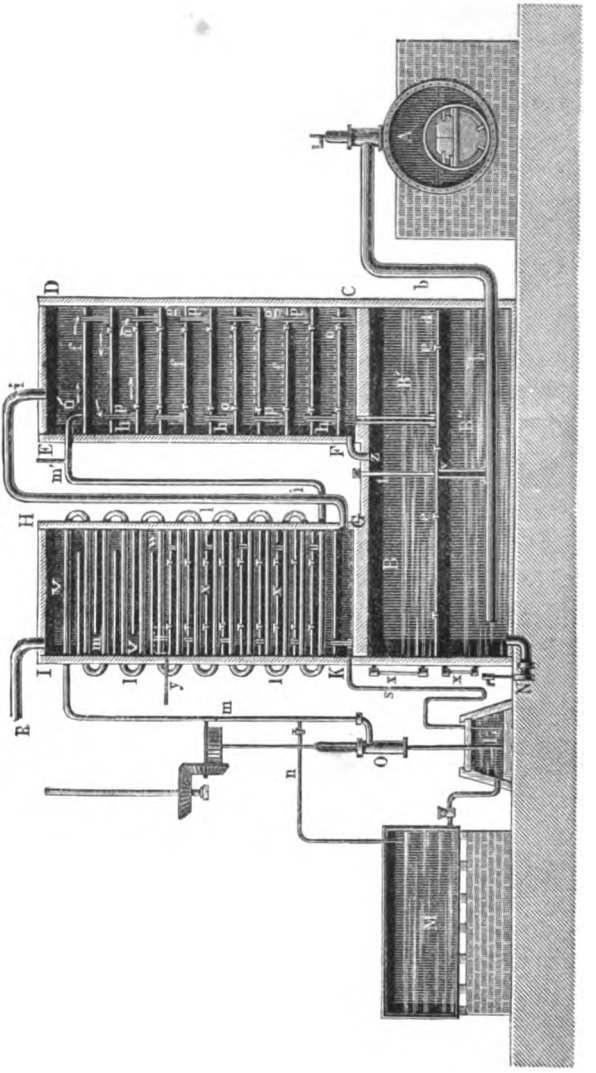
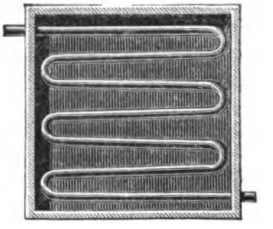


Fig. 155.

chambers, B′B″, by the horizontal diaphragm *d*, which is perforated with numerous apertures for the passage of the vapour, and is moreover furnished with several valves opening upwards, *e e*, in case of more vapour being given off than can escape through the apertures. A pipe *v* reaches nearly to the bottom of B″, where it dips into an hydraulic lute; it can be opened or shut off by a valve attached to the rod *t*, which passes through a stuffing-box at the top. *x x* are liquor-gauges for B′ and B″. The analyzer CDEF is divided into 12 chambers *f f f* by sheet-iron diaphragms *g h*; these also contain many perforations, as well as valves opening upwards, *o o*; also overflow-pipes, *p*, projecting about an inch above each plate, so that a corresponding depth of liquid always remains on each diaphragm. The pipes *p* reach down to the next lower diaphragm, where they dip into hydraulic lutes (traps), so that no steam can escape through them; they are inserted at alternate ends of the diaphragms.

The rectifying-column, GHIK, is in a similar manner divided into 15 chambers. The lower ten of these are filled exactly like those of the analyzer, their diaphragms being furnished with perforations, valves, and overflow-pipes. The top chamber of these ten is covered by a metallic diaphragm with only one large opening at *w* for the passage of vapour, and an overflow-pipe *s*. *w* is surrounded by an upright flange which prevents the return of the most rectified liquid into the lower part of the column. *s* is closed by an hydraulic trap of much greater depth than the others, from which a pipe *y* carries away the condensed but still very hot liquid into a worm or other refrigerator*. The upper five chambers, *v*, are formed by plain unperforated diaphragms, with openings at alternate ends, large enough for the passage of both vapours and liquid; their only use is to cause the vapour to pass along the pipe *m* in a zigzag direction, so as to enlarge the cooling-surface. The pipe *m* runs through all the 15 chambers in a zigzag, as shown in fig. 156, the bends *l l* (fig. 155) forming the connection between the pipes of the different chambers, thus constituting one continuous pipe, leading from the

Fig. 156.



* This can be omitted in rectifying gas-liquor, except when liquor ammoniæ is to be made in the apparatus itself.

pump O upwards, then downwards through all the chambers of the rectifier, again rising upwards outside, and finally ending in the analyzer at *n'*. M is the store-tank for the liquid to be rectified; L, the well for the pump O, which is working continuously and supplies rather more liquor than is necessary to keep the apparatus going; the surplus runs back into M through a pipe, *n*, furnished with a stop-cock by which the operation can be exactly regulated. The necessary heat is supplied by the steam from the boiler A; the steam-pipe *b b* within the receiver B'' branches into a number of smaller perforated pipes (these are not shown in the diagram).

An operation is commenced by setting the pump O in motion, till all the zigzag pipes, *m m*, are filled and the liquor passes into the analyzer at *n'*. The pump is then stopped, and steam is let into the still through *b b*; it passes up through the receivers B'' B', then through the pipe *z* into the analyzer, passes into *i*, in which it descends and enters the bottom of the rectifier at G. It then rises through the chambers X X, envelops the zigzag pipes, and heats the liquor in them. When the attendant by feeling the bends *l l* perceives that perhaps eight or ten of the chambers of the rectifier have become heated, he again sets the pump to work. The gas-liquor, now nearly boiling-hot and always in rapid motion, flows from *n'* into the analyzer and downwards in this through the overflow-pipes *p p* from chamber to chamber, as shown by arrows in the top chambers. It cannot pass down through the perforations of the diaphragms, whose number and size are so regulated that they are no more than sufficient to afford a passage for the vapours upwards when under some pressure. Steam and vapour thus pass in each chamber in numerous jets through a thin stratum of liquor, and so completely expel all volatile ammonium salts that in B no trace of these can be found. When the water-gauge *x* shows that B' is nearly full, the valve at *t* is opened and the contents of B' are discharged into B''. When this is also full its contents are discharged by the cock N, the contents of B' are again run into B''; and in this way the process goes on as long as there is any liquor to be distilled. The boiling-hot spent liquor running from B' serves to raise the temperature of the water intended for feeding the steam-boiler A.

Having now followed the liquor in its course onwards to the point where it is deprived of all volatile ammonia, we will trace the course of the steam. This in its passage through the 12 cham-

bers of the analyzer takes up a large quantity of ammonia, and is partly condensed to water. The remaining mixture of steam and vapour at *i* passes into the rectifier, envelops the pipes *m m*, heats their contents, and by condensation parts with more of its watery portion, which condenses in a boiling state on the various diaphragms. What escapes through *w* is nearly pure ammonia; and this, after being further cooled in *v v* and having lost the last portions of water, escapes through R into the saturator D, fig. 154.

If liquor ammoniæ is to be made, the gas-liquor must be mixed with lime. In this case less steam is blown in, so that the chambers *v v* remain at the ordinary temperature and from the pipe *y* strong liquor can be obtained at will, passing it first, by preference, through a refrigerator. The water condensing lower down in the rectifier contains a little ammonia, and hence runs back through *s* into L, in order to be pumped up again by O.

The operation is mainly regulated by observing the thermometer *m'*, which shows the temperature of the liquor issuing from *n'*. Whenever the liquor is too hot, more liquor is let into the apparatus, or *vice versâ*, which can be effected at will by the overflow-cock *n*.

According to the requirements of a work, Coffey stills are made more or less wide and high, with a corresponding number of steam-pipes and chambers. Such stills hardly pay when less than 10,000 gallons of liquor are worked up per day.

Sometimes they are made much less elaborate than is shown in the above description, plain shelves (up to 60 in number) springing from opposite sides of the tower, and being so made as to retain upon them a thin layer of liquor, the excess of which runs over the free edge of one partition to the next partition below it, and so on to the bottom. Something like this has been once more patented by Brullé and Leclerc (B. P. 1086, 1880).

At another ammonia-works the Coffey stills are from 18 to 25 feet high, 6 to 10 feet long, and 1 or 2 feet wide, with 20 or 30 diaphragms, 3 inches apart; at the top there is a space of 6 inches, at the bottom another of 2 feet (in lieu of the receiver B, fig. 149). Steam of $1\frac{1}{3}$ to 2 atmospheres is employed. The liquor at that works is $7\frac{1}{2}°$ Tw. strong; the solution of ammonium sulphate is boiled down to 52° Tw. before it is allowed to crystallize.

At a third ammonia-works the gas-liquor is distilled in hori-

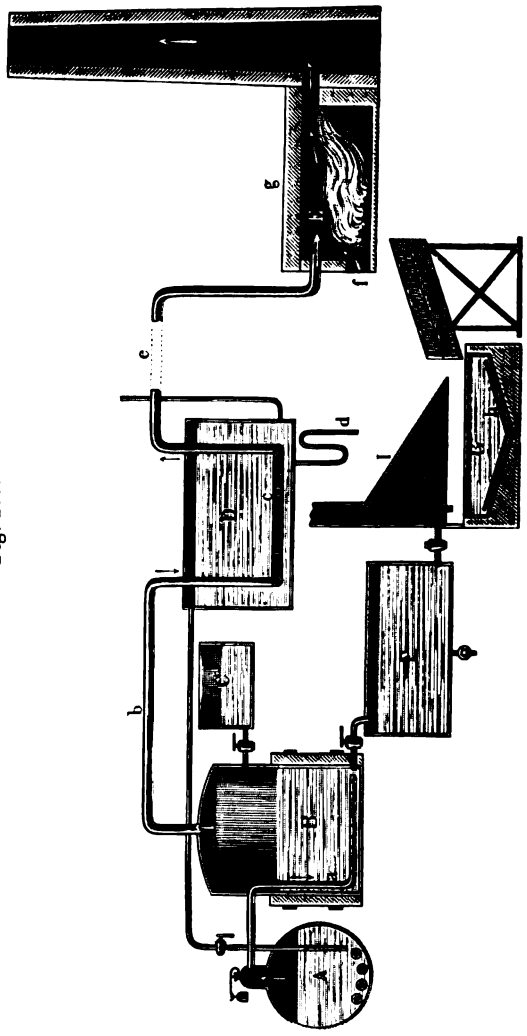


Fig. 157.

zontal cylindrical stills, A (fig. 157), holding 10,000 gallons and charged with 7000 gallons each time. The heat is applied by somewhat superheated steam in a closed coil. It is preferable to employ gas-liquor of not less than 5° Tw., or, say, 10 ounces, without addition of lime. Experience has shown that the loss, including the fixed ammonia, is always 1 ounce per gallon; so that from

a 16-ounce liquor, sulphate equal to 15 ounces is obtained (?). The vapours issue through a lead coil *a*, perforated with ¼-inch holes 6 inches apart, into a lead saturator B, strengthened by planks and hoops (compare p. 599). This is charged with sulphuric acid of 47° Tw. from the tank C, which is filled by means of an air-pressure apparatus (acid-egg)*. The vapours escaping from B pass through the 8-inch pipe *b* into the closed vessel D, where they circulate in the coil *c*; the liquid condensate runs away at *d*. D is filled with gas-liquor, which is thus heated and serves for feeding A. From D the vapours issue at *e*; they are now cooled by air through travelling round the works in a pipe 300 feet long, in which nearly all the water condenses, and are at last conveyed into the furnace E, where a fire is kept up with small coal. Air enters at *f*; and the combustion of the hydrogen sulphide is completed by causing the gases to pass along the red-hot arch *g*. The sulphur dioxide escapes into the air.

The solution of ammonium sulphate from B runs into the settler F (9 × 9 × 2 feet), and from this, through a trap 4 inches from the bottom, into the boiling-down pan G (20 feet long, 5 feet wide, 2 feet deep, half of this being straight, half conical). The heat is applied by means of the steam-coil *h*; the vapours pass away by the hood I†.

Fig. 158 is a sketch of the apparatus in operation at a large London works, where lime is employed and where continuous saturation is preferred. The gas-liquor is pumped at *a* into a column B, which it traverses from the bottom to the top in many pipes, the empty space being filled by the hot gases from the saturator A, which thus raise the temperature of the liquor. The latter now arrives in a square iron column C, about 3 × 3 × 20 feet, packed with retort-graphite. In this the gas-liquor descends, whilst steam enters through *a'* and expels the volatile ammonium salts, which escape at *b*. The liquor passes into D, a small reservoir intended to feed the horizontal still E, in which it is mixed with lime; the steam let into this effects both the agitation and the distillation. The vapours escape at *b'* and unite with those

* Compare Lunge's 'Manufacture of Sulphuric Acid and Alkali,' vol. i. pp. 393 *et seqq.*

† An exact description and diagrams of the steam concentrating-pan, merely sketched here, is given in Lunge's 'Manufacture of Sulphuric Acid and Alkali,' vol. i. pp. 503 *et seqq.*

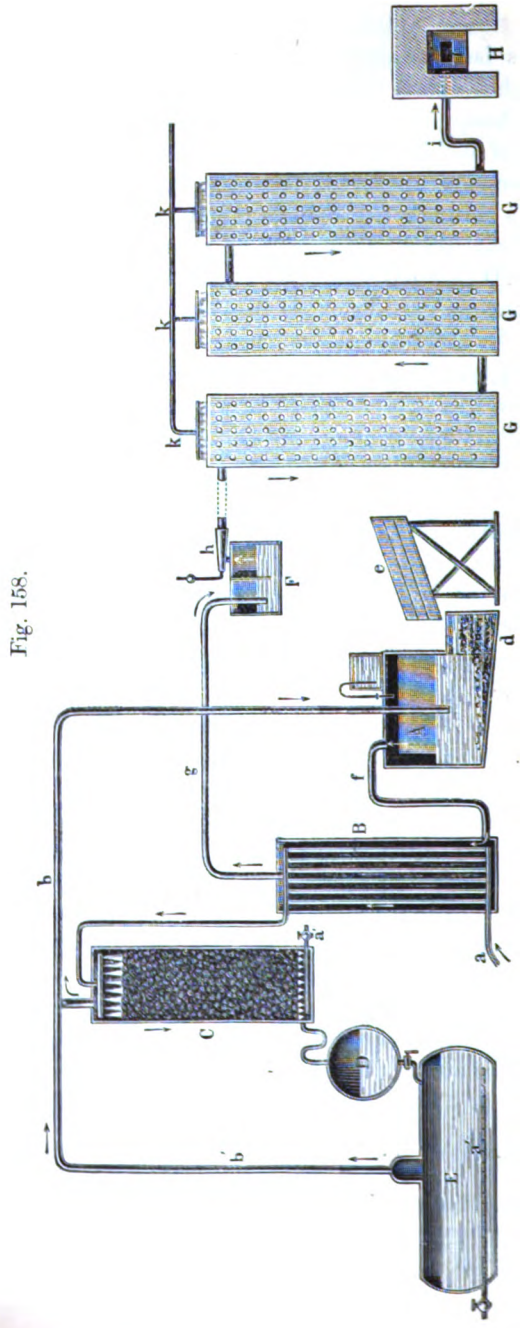


Fig. 158.

from *b* before passing into the saturator A. This is a large lead vessel, continually fed with a thin jet of sulphuric acid of 140° Tw. It is adjoined by the box *d* open at the top; the partition does not reach quite to the bottom, but is always kept luted by liquid. The sulphate of ammonia at once separates in a solid form, is raked out on the sloping bottom of A into *d*, fished out with perforated spades, and drained on the drainer *e*. The mother-liquor always runs back into A; the drained salt at once goes into the market. The hot mixture of steam and gases, escaping from A, first passes through *f* into B in order to heat the gas-liquor (as mentioned above), then through *g* into a vessel F, where it is forced through water by a Körting's blower *h*, and is thus washed and cooled. The complete cooling and condensation of the steam, which would otherwise be a drawback in burning the hydrogen sulphide, is effected in the columns G G G, pierced by numerous pipes passing right across, so that abundant air-cooling takes place; and the liquid can run off below. In summer cold water is run upon these columns from the pipes *k k k*. The cool and dry gas is conveyed by *i* into the furnace H, where it passes through a coke fire, with access of air, and where H_2S is burned into SO_2, as in the former case.

This apparatus seems to be one of the best of the older forms. Each set as described is equal to the production of 100 tons sulphate per week. Recently the burning of the hydrogen sulphide has been given up, and it is, instead, absorbed in ordinary oxide-of-iron purifiers, which, however, do not appear to give full satisfaction.

At a Dutch works I saw the following apparatus. Three horizontal cylindrical boilers are worked in a set. The first two of these receive milk-of-lime, but this is only pumped in after most of the volatile ammonia has been expelled. The gases and steam pass through the third boiler and then into the saturator, which is of the usual form, somewhat resembling fig. 148 (p. 600). The hydrogen sulphide and other noxious gases, given off in the closed part of the saturator, are conducted away in a pipe and are cooled down, first by cold ammoniacal liquor, then by cold water, whereupon they are passed into a small coke fire, above the grate, in order to be burned. The whole saturator, including the open part, is covered by a large wooden hood, from which a pipe leads to the high chimney, so that there is no stench even from the open

part of the saturator. The acid used is = 60° Baumé (sp. gr. 1·71), and the fished-out salt is dried on iron plates, heated from underneath.

Apparatus of A. Mallet.

This apparatus was constructed as early as 1841, but a number of them are still at work at the ammonia-works belonging to the Paris Gas Company, which proves that it must be one of the most serviceable forms of the older type of ammonia-stills. It is represented in fig. 159 in longitudinal section, in fig. 160 half seen from above, half ground-plan, in fig. 161 back elevation. It consists of two similar sets, each of 3 stills, A, B, and C, holding above 1000 gallons apiece, A and B being heated by direct fire. They are provided with agitating-gear H H, passing through glands in the covers, for mixing the gas-liquor and lime and for preventing any burning on. C serves for washing the vapours from B, and is at the same time heated by these. From D the vapours enter a worm, about 70 or 80 feet long, placed in the tank F and cooled by gas-liquor. The liquid here condensed flows into S, and thence into the collector Y. The gases leave the upper part of S and pass through an air-cooled worm T, the pipes U (provided with a safety-apparatus), and into the absorbing-vessel V. The products condensed in T run back into Y.

The gas-liquor, freed from tar, is drawn through the tap *a* into the measuring-vessel G, which at the bottom is connected by a tap with the cooler F; a pipe, branching off at the top, leads to the milk-of-lime pan E. The vessels A, B, C, D are connected at the bottom by the pipes K, L, N, and at the top by the pipes I, J, which reach nearly down to the bottom of B and C. The pipe M takes the milk-of-lime from E into B. Through the pipe O the contents of the vessel Y can be emptied into the vessel D. The pipe P carries to G the vapours given off in the cooler F. Z is a three-way cock, by which the pipes connected with D can be alternately put into communication. In Q is the fire, which first travels round A and then underneath B. R R are lead-covered wooden drainers for the ammonia-salts. X is a leaden tank for the mother-liquors which go back to V.

The saturators are usually made of wood and lined with lead; the ammonia-gas issues through a horizontal lead pipe, lying at

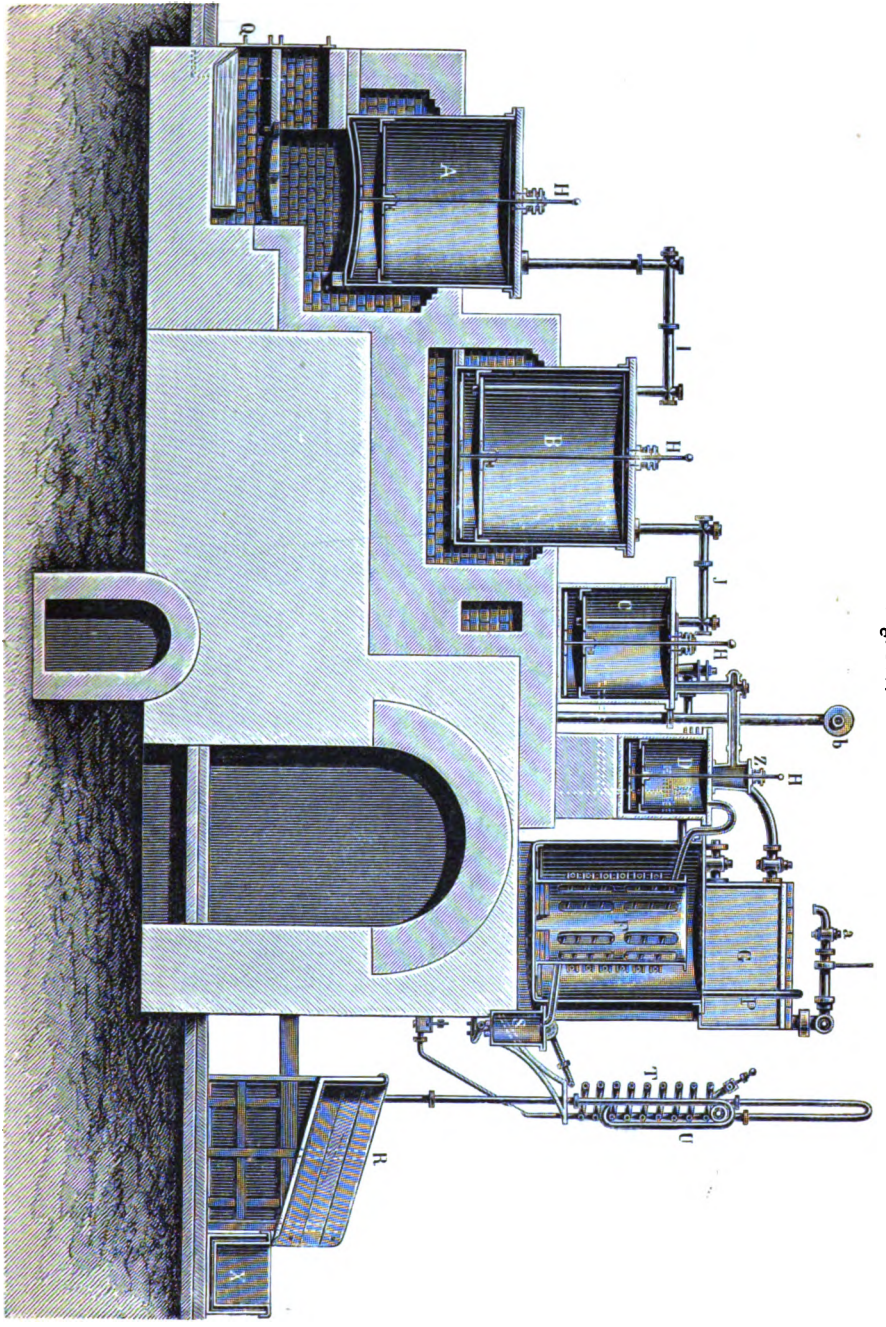


Fig. 159.

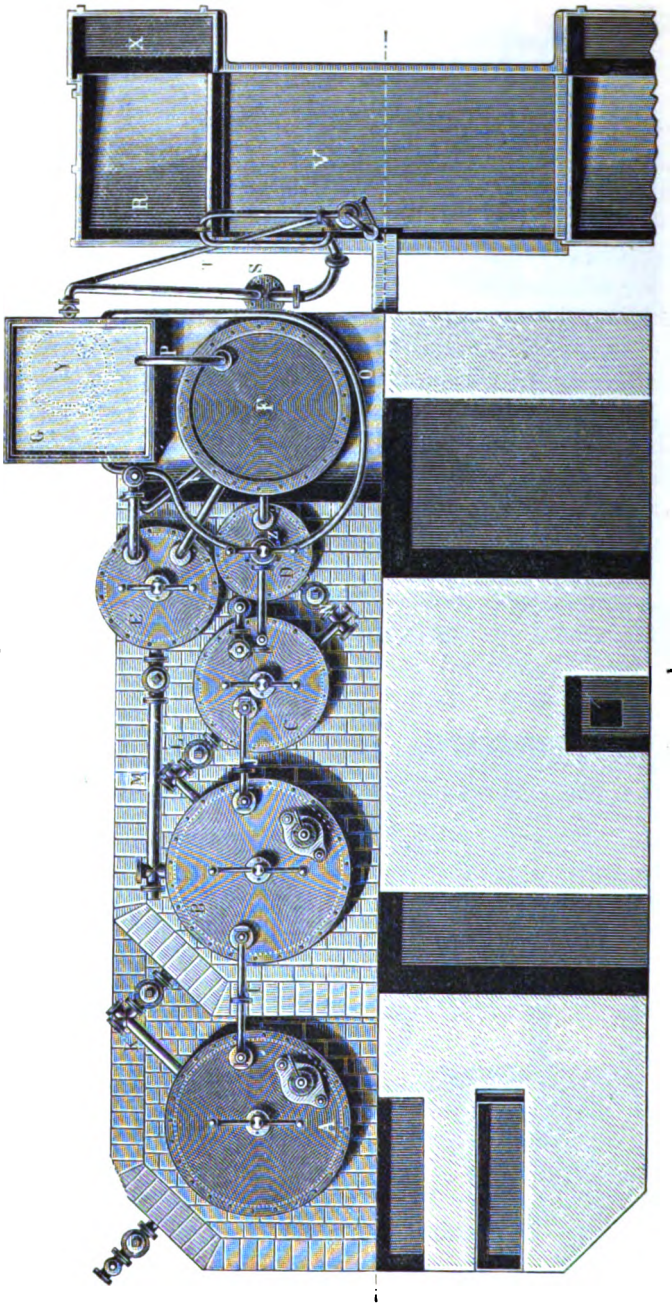
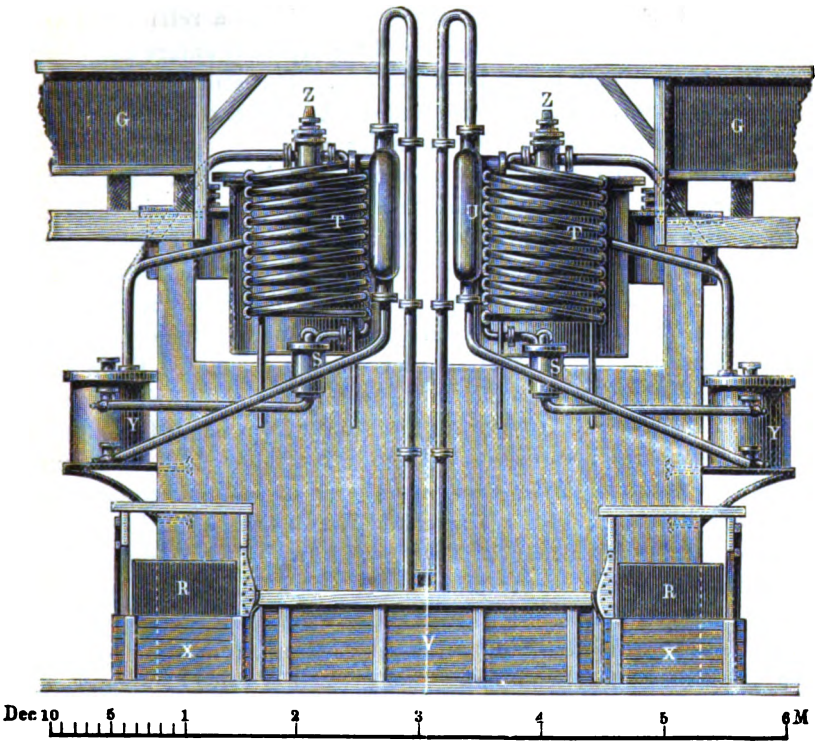


Fig. 100.

Fig. 161.



their bottom, into the acid or the water. The saturator has an air-tight cover; and the non-condensed gases escape through a pipe into the fireplace of a steam-boiler, in order to be burned.

If caustic ammonia is to be prepared, before distillation a quantity of lime sufficient for decomposing all the ammonium salts must of course be put into the still, to avoid contamination of the product [but this cannot be effected by the employment of lime alone!]. For making ammonium chloride or sulphate much less lime is required; and sometimes none at all is employed, the small quantity of fixed ammonium salts being given up as lost. The liquor ammoniæ is only of the crude amber-coloured quality.

In actual practice* only a small portion of the gas-liquor in E

* The following details are unpublished observations of the process as actually carried out at La Villette, Paris.

is mixed with lime, half an hour before the operation; most of the liquor is run from G into F, where it serves as a refrigerant and is itself heated in the process; for this purpose it enters the vessel at the bottom and leaves it at the top. The stills are provided with safety-valves and water-gauges. At the end of the process the liquid is run away into a main drain.

The worm in F is 2 inches wide and has nine coils. The worm T, when, instead of liquid ammonia, sulphate is made, is replaced by a cylinder 10 feet high and 4 feet 6 inches wide, into which the gas-delivery pipe from S enters and passes down nearly to the bottom. This cylinder is kept about one-third filled by means of an overflow-pipe shaped like an inverted siphon; the overflowing liquid is collected in Y, like that coming from S. From that cylinder the gas passes first through an iron pipe, provided with a Welter's safety-tube to prevent any liquid from being forced back by atmospheric pressure, and then into a large lead tank, into which it issues from two lead pipes, lying at the bottom and perforated by many holes. This tank is two-thirds filled with sulphuric acid of 53° B.=116° Tw.*, and provided with a roof-shaped cover, from which the escaping gases (carbon dioxide and hydrogen sulphide) are carried into the chimney by means of a wood conduit. The sulphate crystallizing out is fished out from time to time. drained on sloping lead plates, and dried in a stove or upon metal plates heated by some waste heat.

As soon as a sufficient quantity of liquid has collected by condensation in the vessels Y (say once an hour), the three-way cock Z is for some minutes adjusted so that the gas from D passes no longer into the worm F, but into Y (this is best seen from figs. 159 and 160). Its pressure forces the liquid from Y through O into D; so that no pump is needed for this. The pipe O must reach down to the bottom of Y. Every three hours the contents of A are run off, and those of the succeeding stills B, C, and D run a stage lower down.

Each apparatus is charged with 12 hectolitres (say 270 gallons) of liquor, and 6 operations are made in 24 hours, with an expenditure of about 12 hectolitres of coke as fuel in 24 hours, and of

* When such acid is employed, the temperature of the entering gas must be 80° if the sulphate is to crystallize out continuously.

130 litres of slaked lime for each charge of 1200 litres of liquor. Each cubic metre (or ton) of gas-liquor of 3°·5 Baumé (=8°·5 Tw.) yields 70 kilog. of sulphate; each apparatus therefore about 500 kilog. of sulphate per 24 hours.

At La Villette a daily quantity of 10 tons ammonium sulphate is manufactured in 10 double Mallet's apparatus, and 5 tons liquor ammoniæ in 4 apparatus.

One drawback of this apparatus is, that no proper provision is made for dealing with the hydrogen sulphide; it also contains a number of unnecessary complications, and is undoubtedly inferior to the modern steam-stills of Grüneberg and Feldmann.

A. Mallet later on improved his apparatus by replacing the worm-condensers by upright tubular condensers, similar to those shown in the benzol rectifying-apparatus, fig. 115, p. 450, and by the addition of a rectifying-column, similar in principle to those in use for spirit of wine &c.

Solvay's Apparatus (fig. 162)

is specially intended to obtain concentrated crude liquor for ammonia soda-works, up to a strength of 15° per cent. NH_3. It consists of a still A, divided by partitions C into a number of compartments. Each compartment contains a tank E, connected with the next compartment at the bottom by a pipe. In the upper part of each compartment is fitted a pipe T, which is enlarged below and carries the vapours into the liquid of the next tank. The fireplace is at D. The ammoniacal liquor comes from the store-tank K, and goes first into a small vessel G, in order that the feed may be regulated by means of the valve attached to the lever R and the float X, and enters the still from the pipe M. Suppose this to be filled equally up to the level O. When vapours are evolved by heating the liquor, *e. g.* in B^2, they escape by T and force a certain quantity of the liquid into the annular space between T and E^1, over the margin of E^1 into B^1. Thus a certain quantity of gas-liquor has got from B^1 to B^2 by means of the vapours evolved in the compartment B^2; in the same way the liquid travels from B^2 to B^3 by means of the vapours evolved there: ultimately it arrives in B^{13}, and leaves the last compartment by the pipe U. The progress of the liquid princi-

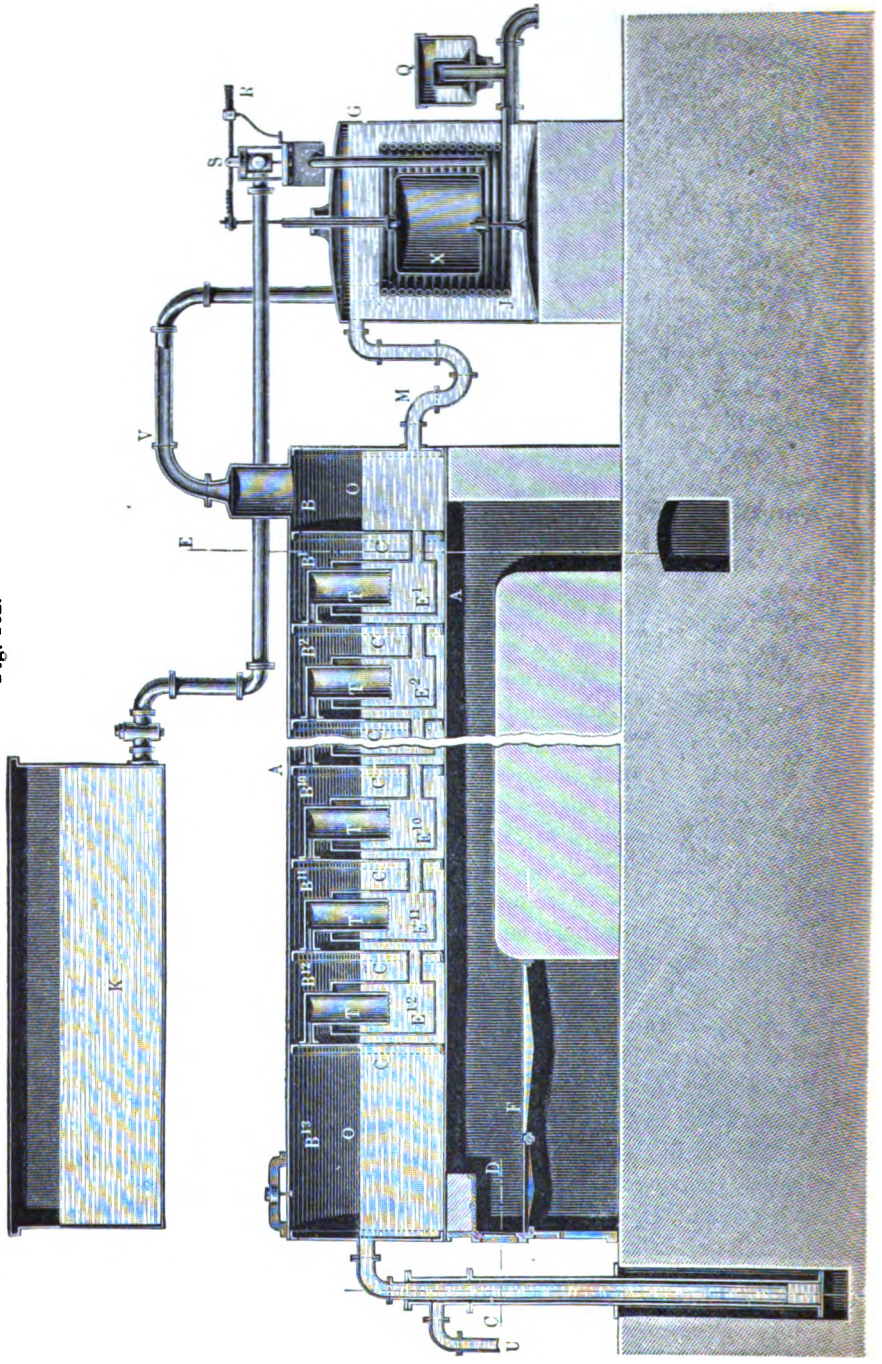


Fig. 102.

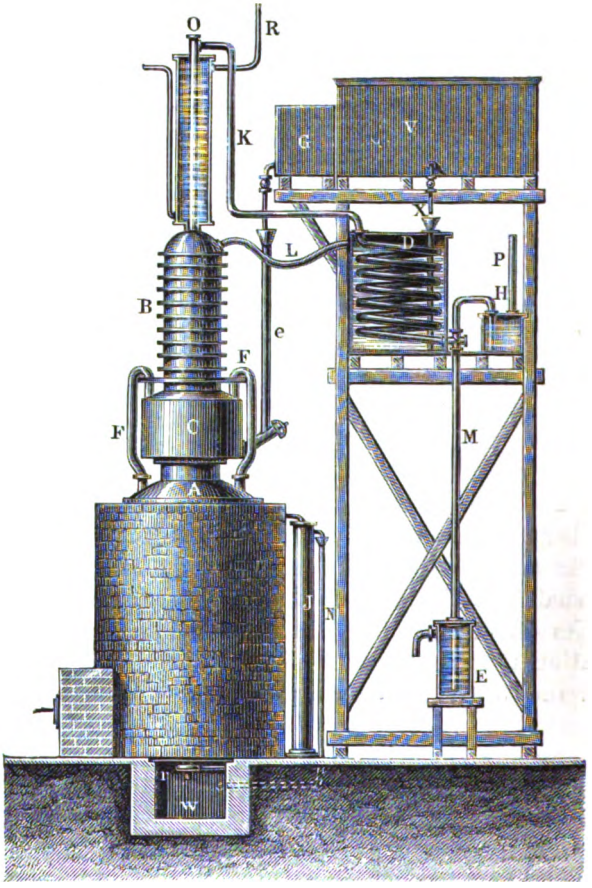
pally depends upon the proportion between the diameter of the dipping pipes T and the vessels E. The vapours arriving in the last chamber B are carried by the pipe V into a worm J, cooled by ammoniacal liquor, and afterwards through a washing-tank Q into the absorbing-apparatus. The float X regulates the feed of liquor into the still; it sinks as the liquid within the condenser is heated by the evolved vapours, and allows a larger quantity of liquor to enter through the valve S if the distillation goes on more quickly. When the firing is interrupted, no vapours are given off, the liquor ceases to pass from one compartment into another, and the level of the liquid rises; at the same time the float rises; and the valve S ultimately shuts off the feed of liquor entirely. According to Hanrez, the dimensions of apparatus hitherto constructed are sufficient for concentrating, every 24 hours, 12, 24, or 48 cubic metres (say tons) of gas-liquor ot two or three degrees Baumé to the above strength, with a consumption of 27 to 36 kilog. of fuel per cubic metre. The hot water running away from U can be utilized for a preliminary heating of cold gas-liquor.

Grüneberg's Apparatus.

One of the best apparatus for distilling gas-liquor is that of H. Grüneberg. His older apparatus (G. P. No. 35, of 1877) has been superseded by a different form (G. P. 5255 and 9392), which alone we shall describe here, as it is most successfully working at 13 factories (September 1880). One of its principal advantages is, preventing the lime from forming hard crusts on the heating-surface of the stills, and removing the lime residue without any loss of time. Figs. 163 and 164 are partly elevations, partly sections. An upright cylindrical still A, heated from the fire-place *g* by flues surrounding it, has within it a vertical cylindrical tube *a a*, the bottom of which, extending below the bottom of the boiler, beyond the heating-zone thereof, is closed and furnished with a blow-off cock, *r*, and a perforated screen. The upper end of this tube, reaching nearly to the top of the boiler, is open to the vapour-space in the boiler. Above the boiler is the vessel C, charged with milk of lime from the tank G

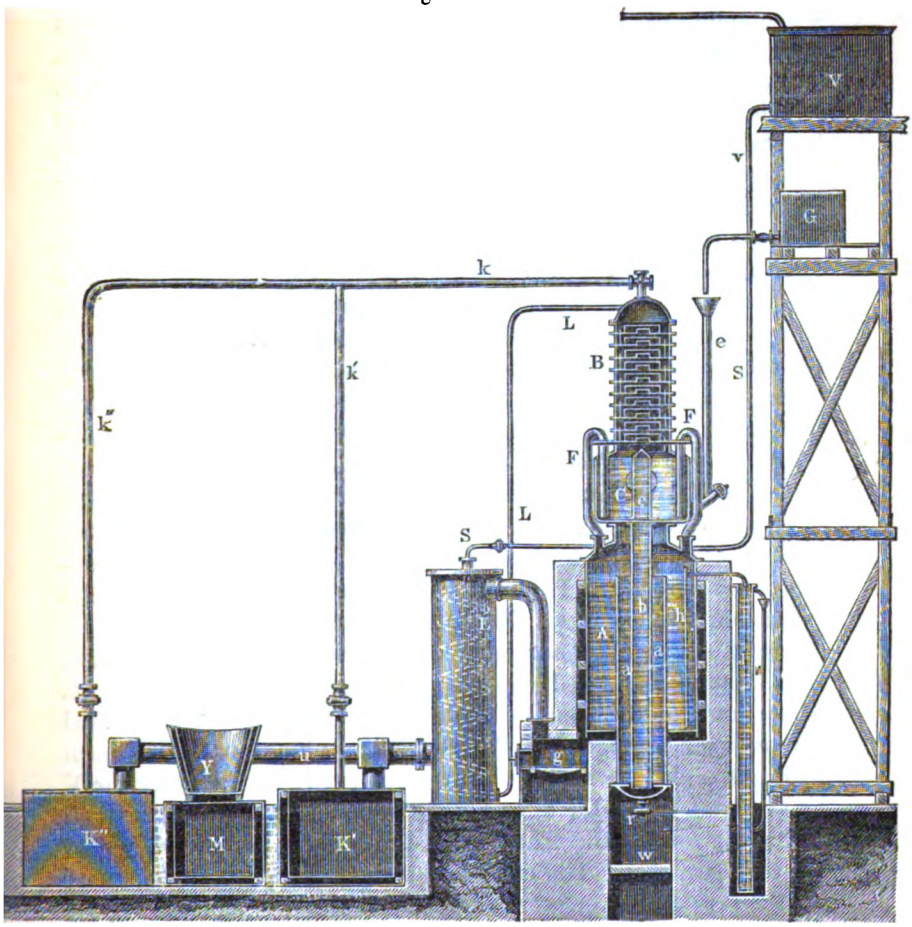
by *e*, and above this a rectifying-column, B, of the description often employed in spirit-stills. The pipes F F extend from the top of A into the lime-vessel, ending near its bottom with numerous small perforations. By these pipes the vapours generated in the still

Fig. 163.



are conveyed into the milk-of-lime, and keep this continuously agitated; they then pass through the successive compartments of the column B. This column is supplied by the pipe L with gas-

Fig. 164.



liquor, which descends from one compartment to another, while the vapours ascending from A through C are intimately mixed with it. Thus the descending gas-liquor is gradually heated and deprived of its volatile ingredients, whilst the ascending vapours are partly condensed and mix with the descending liquid; the uncondensed gases, along with those liberated from the liquid in B, pass away through the pipe *k*. From the bottom of B the liquid, still containing the non-volatile ammonium salts, flows through an opening into the lime-vessel C and is mixed with its contents, the

vapours from F F producing a continuous agitation. Here the ammonium salts are decomposed, and part of the ammonia passes along through B into *k*. The liquid, still containing ammonia, passes, by the overflow pipe *c b*, to the bottom of the boiler-tube, *a*, which is removed from the direct action of the fire, so that there is no danger of the lime becoming attached to the surface of the tube, neither can the material of the tube, or that of the lime-vessel, be injured by overheating.

From the bottom of the tube *a* the liquid rises through the perforated plate *d*, flows over into the outer boiler A and is heated in the same; the gases and vapours evolved are conveyed by F F into C, as above mentioned. From the bottom of A the liquid, now entirely deprived of ammonia, overflows through *h* into a deep vessel J, the contents of which operate as an hydraulic seal, and from this through N to a drain. All this proceeds *continuously*—the feeding with gas-liquor by L, the overflowing of the spent liquor by N, and the escape of the ammoniacal vapours at *k*.

The apparatus fig. 163 serves for producing a concentrated solution of ammonium carbonate and sulphide, *e. g.* for the ammoniacal soda process. The vapours rise through the cooling-pipe O into a worm in the vessel D, where they are condensed to the condition of (impure) liquor ammoniæ. This flows into a vessel E, whilst the uncondensed vapours and gases pass into a vessel H, whose contents form an hydraulic seal. The gas not condensed here escapes through P. The vessel D is closed; and the worm within is cooled by raw gas-liquor supplied from the reservoir V by the funnel-pipe X; after getting heated here, it passes through L into the column B. The cooling-pipe O acts as a regulator of the concentration. The more cold water is supplied to its casing by the pipe R, the greater is the condensation of aqueous vapour in O, the condensed water flowing back into B, and the more concentrated is the residual fluid which passes to the worm in D. Thus the degree of concentration of the liquid ammonia can be regulated at will.

If it were intended to make real liquor ammoniæ, the vapours issuing from the column would have to be passed through a number of vessels filled with milk of lime and finally into a cooled absorbing vessel.

The apparatus fig. 164 serves for producing ammonium sulphate. The gaseous mixture passes through *k* and alternately *k'* and *k''* to the saturators K' and K'', containing sulphuric acid. Considerable

heat is evolved by the combination of this acid with ammonia, so as to vaporize the excess of water present in the acid [provided the latter be not much under 130° Tw.]. The vapour thus generated, together with offensive gases (CO_2, H_2S, &c.), pass along the large pipe *u* and into the vessel E, where their heat is utilized for a preliminary heating of the gas-liquor which passes at S into a coil or set of pipes, in order to be conveyed through L into the column. From E the uncondensed gases pass through *v* into a fire-place *g*, where the offensive gases are consumed. The ammonium sulphate separated in K′ and K″ is put into the drainer Y, provided with a perforated false bottom; the mother-liquors collect in M.

The coal used averages one cwt. for each ton of gas-liquor passed through the apparatus; the lime, 15 or 20 per cent. of the ammonium sulphate produced. Two men can attend to an apparatus capable of distilling ten tons per diem. Such an apparatus, without the lime-vessel, is 10 feet high and 5 feet wide; the column and lime-vessel add another 8 feet. It costs from £175 to £200.

Some minor improvements of Grüneberg's apparatus are contained in the German patents No. 15446 and 18852.

The following practical experiences with Grüneberg's ammonia apparatus have been described by Kunath and Blum *. At Danzig such an apparatus was erected at a cost of about £400, including alterations to a shed and erection of a chimney. A twelvemonths' working yielded :—

Income.

		Mark.
57508·5 kilog. ammonium sulphate		22315·82
Expenditure.	Mark.	
Interest on M. 8000 at 5 per cent. ...	400·00	
Amortization	400·00	
59748 kilog. sulphuric acid, ½ 106°, ½ 142° Tw.	5468·63	
11000 kilog. lime	427·00	
7537·5 kilog. coke	150·75	
191 hectolitres coke-breeze	57·30	
117 hectolitres small coke	5·85	
Wages, packages, &c.	1173·34	
Repairing a saturator.....	8·00	
		8090·87
Profit		14224·95

* Wagner-Fischer's Jahresb. d. chem. Technol. for 1884, p. 311.

Each ton of coal distilled produced 6·24 kilog. of finished salt.

At Graudenz, with a yearly production of 5500 kilog. of ammonium sulphate, the expenditure is calculated per 100 kilog. at :—

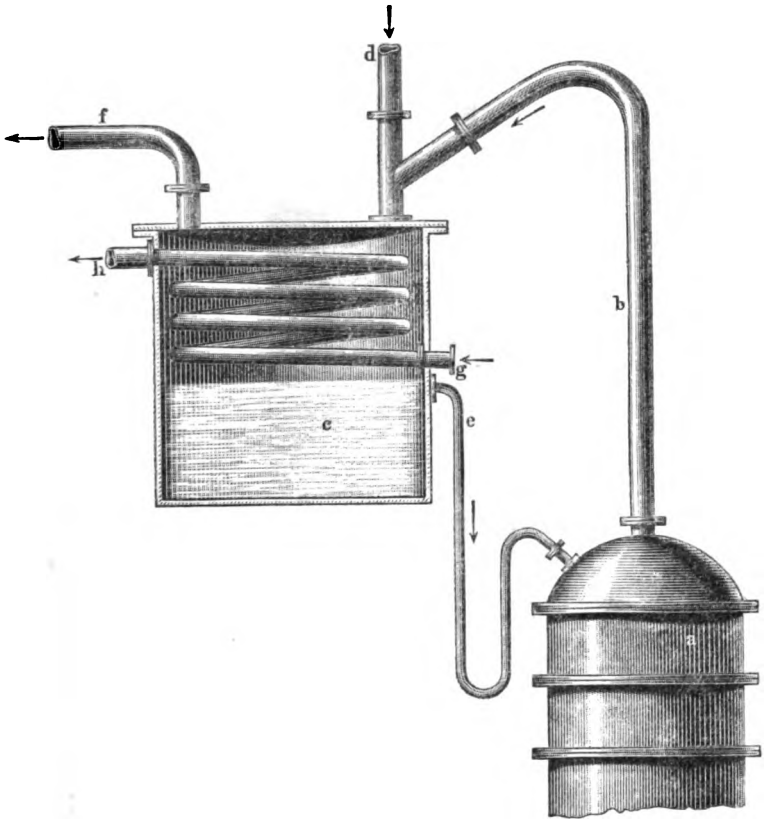
	Mark.
100 kilog. sulphuric acid 142° Tw. ...	9·00
100 kilog. coal	1·60
20 kilog. lime	0·40
Packages	0·50
Wages and management	3·00
Repairs	2·00
Carriage, &c.	1·00
Amortization and interest	6·00
	23·50

The author owes the following further statements to the kindness of Dr. Grüneberg. The two boilers A and C are now made in one piece, of cylindrical form. The lime is now introduced as sifted milk-of-lime by a membrane-pump. The milk-of-lime reservoir is an oblong iron tank with a vertical division, consisting of a fine sieve. The crude gas-liquor is now gradually heated in the following way, as shown in fig. 165.

a is the top of the column, *b* the gas-pipe, *c* the liquor-heater; *d*, inlet for cold gas-liquor; *e*, overflow of the same and conduit into the column; *f*, outlet pipe for the cooled gas. When heating the liquor in this way, the acid employed in the saturation must be of sp. grav.=142° Tw. If weaker acid (106°) is to be employed, the heating of the liquor must be produced by the waste heat of the gases from the saturator, in order to have a sufficient evaporation in the same. If the object is making concentrated gas-liquor, the gases must be cooled as much as possible, and for this purpose there is on the upper part of the vessel *c* a worm *g h*, through which cold water is constantly running.

The worm D in fig. 163, which is sometimes stopped up by crystallizations of ammonium carbonate, has now been replaced by a cooler, acting both inside and outside, as shown in fig. 166. L is an annular iron vessel, fixed in the outer cylinder M. The ammoniacal vapours enter at *o*, condense in L, and the condensing-liquor runs off at *p* into an hydraulic seal, whence it runs over at *q* into the vessels intended to carry it away. The cooling-water

Fig. 165.



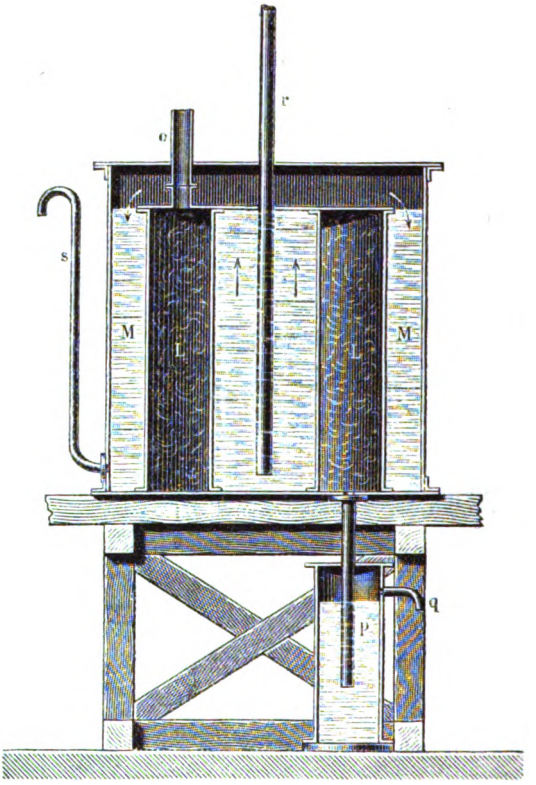
enters through *r* at the bottom of the vessel, runs over the annular cooler L, and is carried off from the outer part of M by *s*.

A complete apparatus for sulphate of ammonia with lead saturator, liquor-heater, &c. for 10 tons gas-liquor now costs 3500 Mark (= £175). There are more than 50 at work now.

While the older Grüneberg stills are adapted to direct firing, a new modification has been patented by Grüneberg and Blum (G. P. 33320), which seems preferable in all cases where there is steam at disposal *. Fig. 167 shows the apparatus as adapted to the manufacture of sulphate of ammonia. A is the still, B the

* English agent, Henry Simon, Manchester.

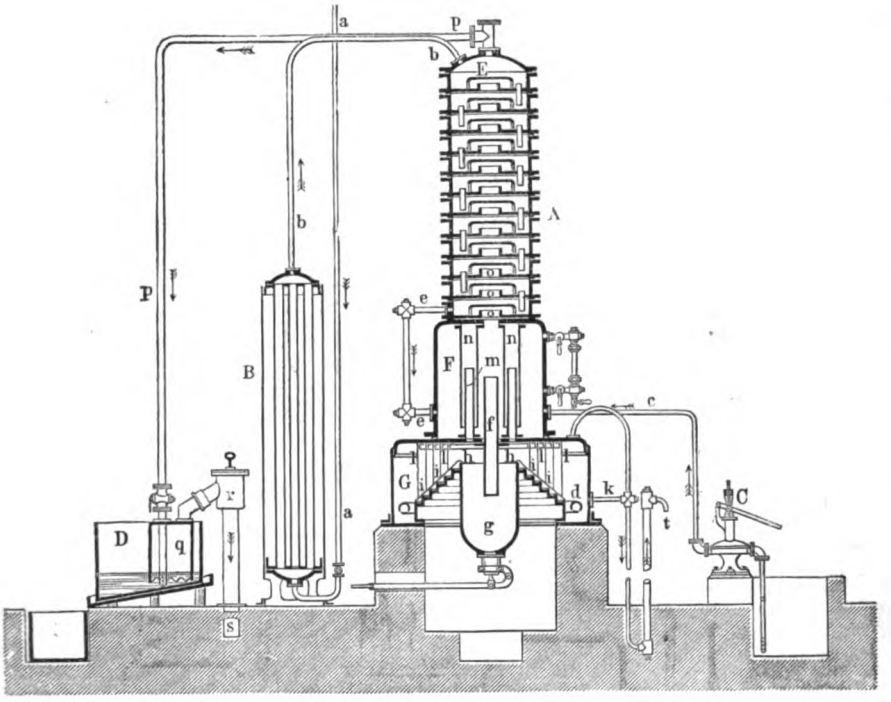
Fig. 166.



gas-liquor heater (economizer), C the lime-pump, and D the saturator. The gas-liquor enters the heat-economizer B by means of pipe *a*, and after from this it runs by pipe *b* into the column E. The still A unites the three parts of the old apparatus in one piece. The upper column E serves to drive out the volatile ammonium salts; the lime-vessel F, into which milk-of-lime is pumped by means of pump C and pipe *c*, serves for expelling the fixed ammonia; and the boiler G, with its peculiarly stepped cone, serves to boil the liquor in thin sheets, by means of the steam-coil *d*, and thus to set free the last portions of ammonia.

In the economizer B the first heating of the liquor takes place by means of the hot vapours (noxious gases) from the saturator D, which ascend through the bell *q*, the pipe *r*, and the inner pipes

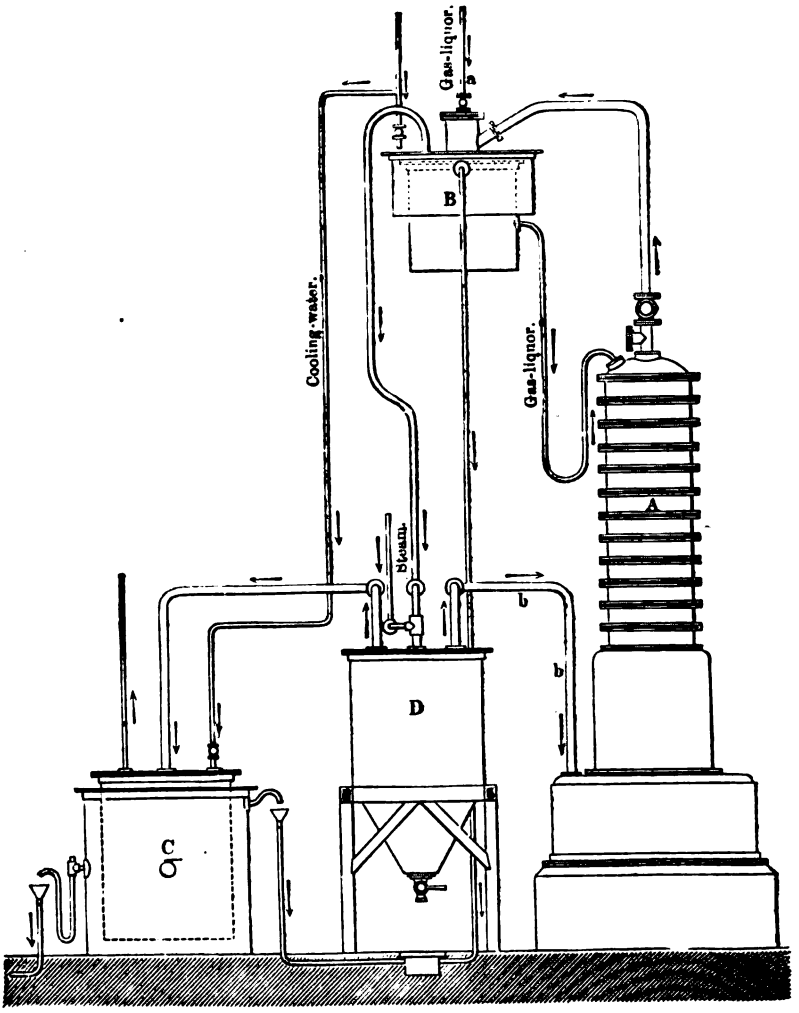
Fig. 167.



of B, while the liquor, arriving at *a*, rises up in B. It then enters, through pipe *b*, at the top of the still A into the dephlegmating column E, and finds its way downwards from chamber to chamber, till it gets into the lime-vessel F by means of pipe *e*. From here it overflows by pipe *f* into the sludge-catcher *g*, overflows here again all round at *h h*, and runs over the cone *l* downwards from step to step; from the pipe *k* it is discharged continuously, and quite spent, to the overflow *t*.

The steam travels in the opposite way to the liquor, namely, along the steps of cone *l*, upwards in pipe *m*, and through *n* into the lime-vessel F. From here the mixed steam and ammonia-vapours ascend into the column E, and traverse this from chamber to chamber, and ultimately leave it by the pipe *p*. This pipe enters the saturating-box D, filled with sulphuric acid. The noxious gases collecting in the bell *q* are led through the pipe *r* and the flue *s* into the economizer B, where they give up their

Fig. 168.



heat to the crude gas-liquor, and lose their steam in the shape of condensed water. Ultimately they are conveyed, by a pipe not shown in the diagram, into some fireplace, to be burned, or can be treated in any other desired way (p. 612 *et seq.*).

The essential feature of the Grüneberg-Blum apparatus is the

stepped cone. The liquor in descending this is more and more spread out, and ultimately meets the ascending steam as a fine spray; thus the last traces of ammonia are set free. In the most recent form of these stills the milk-of-lime vessel is made to surround the cone, and thus to keep the heat in as much as possible.

The apparatus fig. 168 serves for making concentrated gas-liquor, and as intermediary apparatus for making liquor ammoniæ. In this case the gas-liquor enters into the vessel B by means of the tube *a*. Vessel B serves the double purpose of cooling the ammonia-vapours coming from the still A, and of heating-up the gas-liquor entering through *a*. From here the liquor is conveyed by means of a siphon-pipe into the top of the still A. The cooled-down ammonia-vapours coming out of B are now either conveyed directly into the cooler C, constructed like that shown in fig. 166 (where, by means of cold water in the inner and the annular outer space, the vapours are condensed and Concentrated Ammoniacal Liquor is obtained), or else, if very concentrated liquor (up to 24 per cent. NH_3) is required, the vapours are first passed from B through the lime-vessel D, and only then into C. The (two) lime-vessels D serve to remove the carbonic acid and sulphuretted hydrogen, and are indispensable intermediary links for the manufacture of liquor ammoniæ; but they are equally indispensable when a concentrated crude liquor from 18 per cent. NH_3 upwards is to be manufactured, since above that strength ammonium carbonate would crystallize out; and hence a higher concentration would not produce a liquid, but a pasty mass, unless the CO_2 and H_2S were removed, which has not been the case in the upper part of the still A, no lime being present there. There are two such lime-vessels D arranged side by side, so that when the lime is spent in one of the vessels, the vapours, by changing the position of cocks, can be at once passed into the other vessel. When this change has been effected, steam is then blown into the first vessel, in order to drive out the ammonia contained therein, which is sent back to the still through pipe *b*. The vessel is now emptied and charged again with fresh lime, to be ready whenever the second vessel shall have done its duty.

The apparatus specially intended for making pure liquor ammoniæ will be described under that heading.

These ammonia-stills are made in six different sizes, to distil from 1300 to 6600 gallons of gas-liquor per 24 hours. According

to trustworthy testimonials, they answer very well indeed: the ammonia left in the liquors is, on the average, not above 0·05 per cent.; there is but a small consumption of steam, very little labour, no nuisance, and no trouble.

Watson Smith gives the following calculation for distilling in a Grüneberg-Blum still the gas-liquor obtained in carbonizing 35,000 tons of coal, viz. about 3500 tons of liquor at 5½° Tw.*:—

	Tons.	Price. s. d.	£ s. d.
Sulphuric acid 142° Tw.	389	40 0	778 0 0
Lime	71	12 6	44 7 6
Labour, 4 men 50 weeks, @	...	25 0	250 0 0
Coal	175	8 0	70 0 0
Casks and packing	...	.....	155 12 0
Sundries, repairs, &c.	...	.....	116 14 0
Depreciation on plant, £300, buildings £150: total £450 @	...	10 p. c.	45 0 0
Interest on plant and buildings £450, land £100: total £550 @	...	5 p. c.	27 10 0
Gas-liquor 5½° Twaddell	3500	12 0	2100 0 0
Total cost of manufacturing			£3587 3 6
	Tons.		
Produce, sulphate of ammonia	389	£11	4279 0 0
Deduct cost of manufacture	...	.....	3587 3 6
Profit	...	.....	£691 16 6

Feldmann's Apparatus.

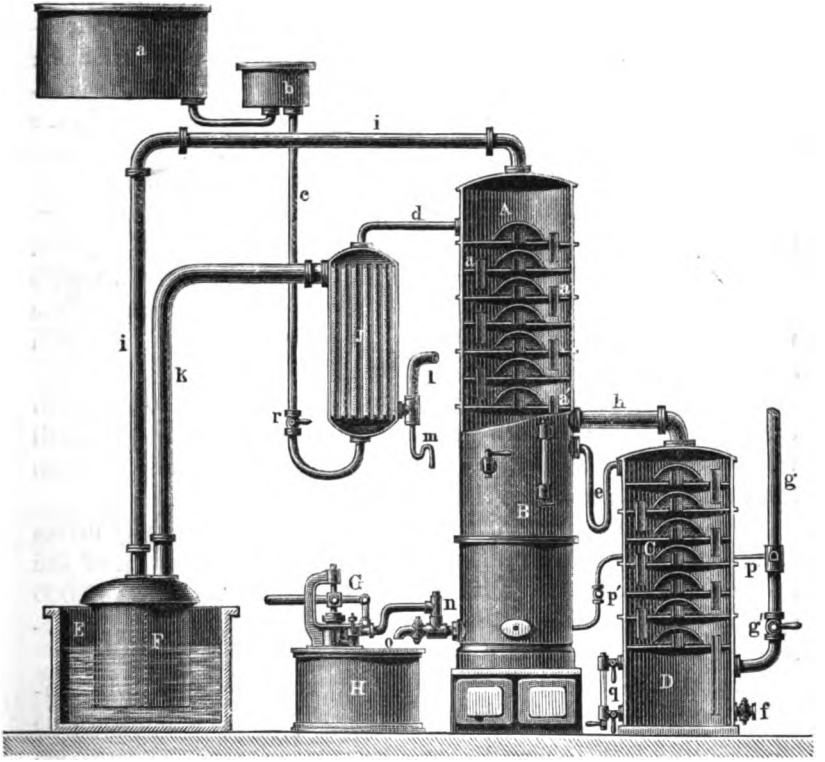
Dr. A. Feldmann, of Bremen, has constructed an ammonia-still (G. P. 21708; B. P. 3643, 1882; English Agents, Schwab and Overhoff, Manchester), which is very much recommended, and of which, in May 1886, there were 48 at work in different countries. It is a steam-still, and is adapted for making sulphate, liquor ammoniæ, or concentrated gas-liquor. Its principle is that of a continuously acting column where not merely the volatile ammonia, but also the fixed ammonia, set free by lime, is driven off. Otherwise the principle of the dephlegmation-column is the same as that adopted in the Coffey still, the Grüneberg still, and many others.

Considering its great capabilities, the apparatus requires but little room for setting up. An apparatus to distil from 8 to 10 tons of ammoniacal liquor in 24 hours occupies a space of 17 feet by 13 feet by 10 feet.

* Industries, 1886, p. 242.

The apparatus consists of the column A, the decomposing-tank B, and the column C. The ammoniacal liquor flows from the feed-tank *a* into the supply-tank *b*, the object of which is to obtain a regular flow into the column through pipe *c* into the tubular boiler J, and thence through *d* into the top chamber of column A. From here it passes through the overflow-pipes *a* from chamber to chamber, in each of which it is boiled up by the steam which

Fig. 169.



fills the stills, and is delivered free from all volatile ammoniacal compounds, through a long overflow-pipe *a'*, almost at the bottom of the decomposing-tank B. Into this tank milk-of-lime is introduced through the pump G, and the inflowing gas-liquor is constantly mixed by a steam-agitator. The inlet of steam is so regulated that the decomposed gas-liquor must run out at the top of tank B; and by the working of a sieve, introduced to break

the ebullition, it passes purified and freed of surplus lime through siphon *e* into column C. In the separate chambers of this column, the ammonia formed is driven out, the spent liquor collects in the part D, and flows constantly through the tap *f*. The steam required for distilling is admitted through pipe *g* into column C; traversing the fluid in each separate chamber, it passes through pipe *h* and tank B into column A. It then rises through all the chambers in A, and leaves, charged with accumulated ammonia, by the exit-pipe *i*. Finally it arrives under the leaden bell F, which is partly submerged in sulphuric acid, contained in the lead-lined cistern E. The ammonia combines with the sulphuric acid; the gases which have not been absorbed, carbonic acid, sulphuretted hydrogen, &c., mixed with steam under the leaden bell, are conducted through the exit-pipe *k* into the cylinder J. The action of this cylinder is exactly similar to that of the economizer in Grüneberg's apparatus, so that we need not repeat its description in this place; nor need we go into the treatment of the gases. The essential difference between Feldmann's and Grüneberg's apparatus consists in this: that the former, after driving off the volatile ammonia, saturates the liquor with lime, and sends it in a *clear* state through a second column.

The usual sizes of the apparatus are for distilling 5, 10, or 15 tons of ammoniacal liquor per day; but it can be made to distil very much larger quantities. At Silvertown there is a still for 80 tons, and at Runcorn one for 200 tons liquor per day.

This apparatus (according to reliable information) easily drives off the ammonia to such an extent that the distillation test of the residues does not show more than 3 to 5 parts NH_3 in 100,000 parts of liquor; and the liberation of the NH_3 can be made practically absolute.

A very striking example of the difference between the old two-boiler system with direct firing and the rational new apparatus is afforded by a return made by the Bielefeld Corporation Gas-works. Formerly they worked only 2½ tons liquor in a two-boiler apparatus with direct firing. The result of 100 days' working was 466 cwt. of damp, greenish sulphate, with barely 20 per cent. nitrogen. The wages per cwt. of sulphate amounted to 0·91 Mark, the consumption of coke to 2·87 Scheffel=0·86 Mark. After putting up a Feldmann still the daily consumption of gas-liquor was raised to 7½–8 tons; the yield of sulphate upon the coal

treated in the retorts was 0·9 per cent. The output of 63 days' working was 684 cwt. of nearly white sulphate, with 20·68 per cent. nitrogen. The expenses were as follows per cwt. of sulphate:—

	Mark.
82·6 lb. sulphuric acid, 168° Tw., @ M. 4 per cwt.	3·30
1·5 Scheffel coke @ 0·30	0·45
Wages (@ 4·25 mark per diem)	0·40
Lime	0·15
Sundries (lighting, shovels, &c.)	0·15
Amortization and interest	1·00
	5·45

Feldmann claims* that his apparatus obviates the difficulty of obstructing the column by a precipitation of lime and lime-salts in a much simpler way than is done by P. Mallet (see further on); and that the employment of a column for expelling the fixed ammonia permits not merely doing this in the most perfect possible form, but also with a minimum of steam. This is most important when utilizing the gas-liquor for manufacturing sal ammoniac, where there should be as little subsequent evaporation as possible; but it is also very useful in making sulphate of ammonia, because it greatly facilitates the dealing with the sulphuretted hydrogen.

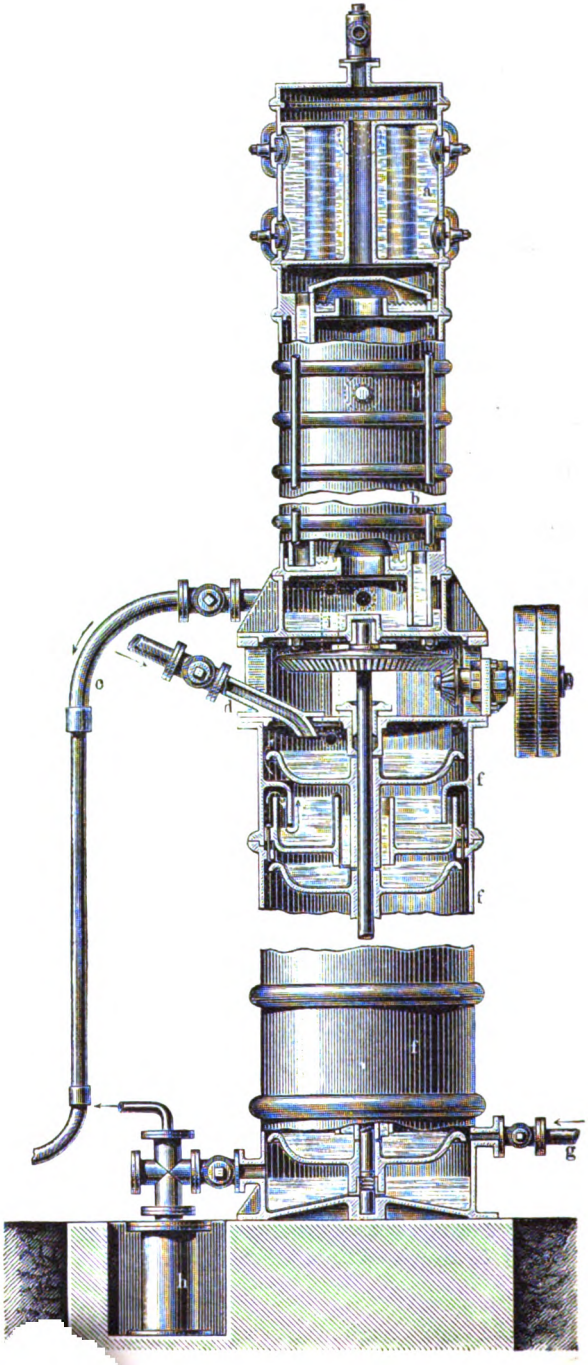
P. Mallet's Apparatus (1884).

P. Mallet† has set himself the special object of making an "inobstructible column" for distilling ammoniacal liquor in contact with lime, without having to clarify it by repose (as is necessary especially for liquors produced in the treatment of sewage), or without having to relegate the lime treatment to another vessel. His apparatus is shown in fig. 170. An ordinary column *b b*, surmounted by an "analyzer" *a*, serves to expel the volatile ammonia. From here the liquor runs off by *c* into the apparatus (fig. 171) intended for mixing with lime. This consists of a closed hopper *k*, which is charged with a sufficient quantity of quicklime to serve for several hours, and of an endless screw *l*, which conveys this lime to the mixer *m*; here it is mixed with the liquor entering at *c*, which slakes the lime, and carries it in a state of suspension through the pipe *d* into the inobstructible column. The

* Journal für Gasbeleuchtung, 1885, p. 768.

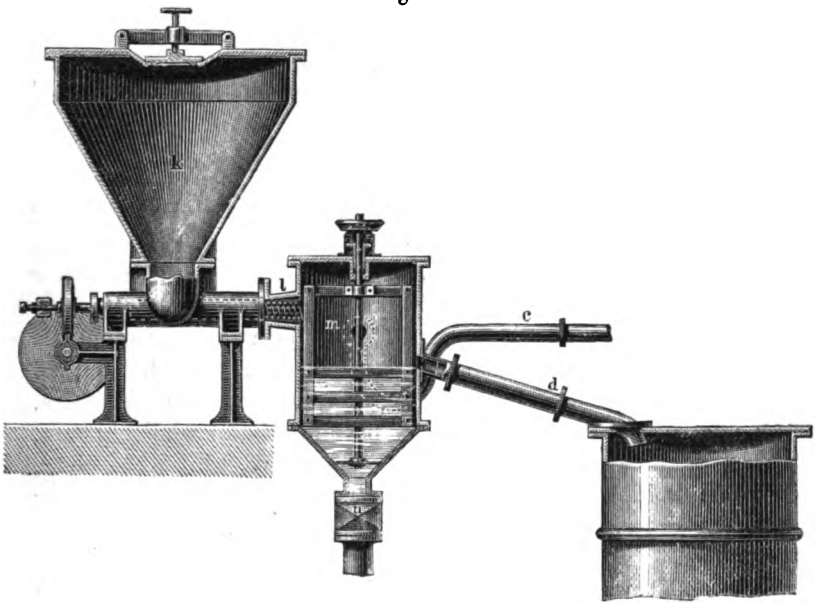
† 52 Boulevard de la Vilette, Paris.

Fig. 170.



valve *n* serves for removing from time to time unslaked pieces, stones, &c. The mixture of lime and liquor now descends the lower column *f* (fig. 170) from plate to plate; the revolving shaft in the centre of this column, by means of scrapers fixed to it in each of the chambers of the column, keeps the lime suspended in the liquor and prevents any crusts forming on the plates. The spent liquor is cast out by the mechanical purger *h*; for very dirty lime a sludge-box must be provided, from which the deposit is taken out from time to time.

Fig. 171.



A special advantage claimed for this apparatus is that it works with quicklime and utilizes the heat of slaking, at the same time dispensing with the necessity of sifting the milk-of-lime; but it does not appear that this is a feature essential to the "colonne inobstruable," whose principal speciality, the revolving shaft, is evidently not without its drawbacks. Many manufacturers will prefer a simpler apparatus, dispensing with machinery.

Apparatus specially intended for working Ammoniacal Liquors from Sewage.

A considerable number of these are described by C. Vincent in

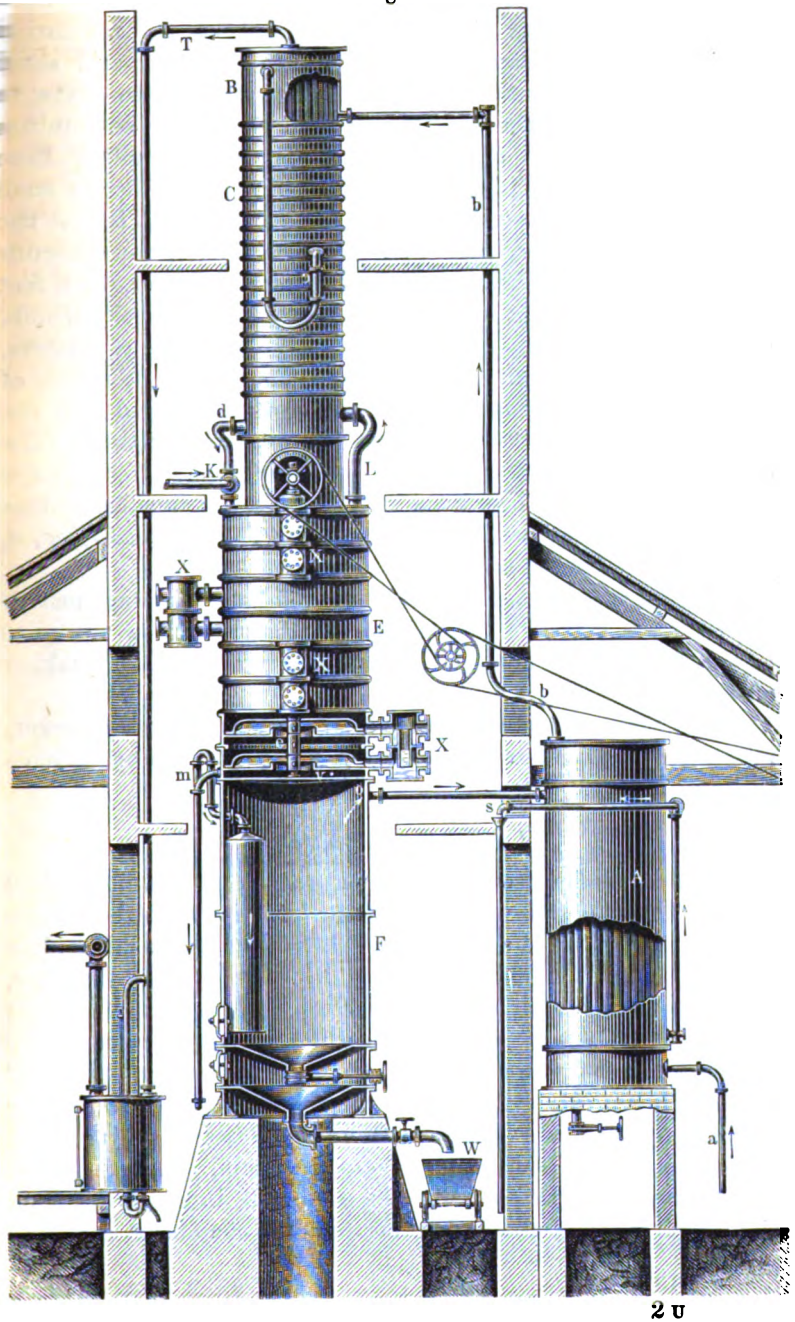
the 'Encyclopédie Chimique,' 2nd section, tome x. part 4, pp. 14 *et seq.*; but most of them present nothing calling for special recommendation, as the older apparatus of Figuera, of Margueritte and Sourdeval, and others; or else they are only various forms of combinations of boilers with dephlegmating-columns and heat-economizers, not different in principle from those already described, as the apparatus of Lair, of Sintier and Muhé, &c. That of Hennebutte and Vauréal has a very peculiar form, but the principle is always the same. We would refer for descriptions and diagrams of these apparatus to M. Vincent's book; also for that of Chevalet's apparatus for treating turbid sewage and "tout venant," that is, the whole contents of the sewers, including night-soil and all other solid refuse. We will, however, describe two other apparatus constructed for the same purpose.

P. Mallet's Apparatus for treating Thick Sewage

is shown in fig. 172. It consists of a tubular heater A; a tubular vapour "analyzer" B; a cast-iron column C, 4 feet 8 inches wide, serving as dephlegmator. This column, by means of a hollow stand, rests on the top of the agitating-column E. The latter has a diameter of 6 feet 8 inches, and contains a number of plates with central holes; a central shaft, made to revolve by toothed gear, carries a set of stirrers ranging over every one of these plates. The sludge-decanter F forms the bottom of the whole system. The sludge itself is discharged into trucks W, whilst the clear, decanted, boiling part of the spent liquor passes on to the heater A, and afterwards, being completely cooled down, runs off through the tube *s*.

The fresh sewage matter is forced by means of a pump through the pipe *a* into the heater A, and passes through its tubes; on its way it gets heated by the spent liquor, circulating in the inverse direction, before issuing at *s*. The sewage then ascends through the 4-inch pipe *b* into the analyzer B, in which it is further heated by the vapours ascending from the rectifier C; it then passes out by the siphon-tube *c* into the column C at its tenth chamber, and descends in this, in order to pass through the tube *d* into the agitating-column E. During this transit the volatile ammonium salts contained in the sewage are carried off by the hot vapours coming from E and escape through L; the vapours pass through

Fig. 172.



the rectifier C, where they become richer in ammonia, then through the analyzer B, where they give up the remaining water, and at last escape through T into the sulphuric-acid saturator. The uncondensable gases are carried under a fire-grate, to be burned. Before the sewage, deprived of volatile ammonium salts, enters through *d* into E, it is mixed with milk-of-lime pumped in through K, in the proportion of 8 kilog. lime to each ton of sewage. The action of the agitating-column E is just the same as has been described, p. 655. The spent matter now descends through the siphon-tube, *m*, into the sludge-decanter, F, 6 feet 8 inches wide, where it suffers an enormous loss of velocity which, along with the action of the lime on the albuminous matters, promotes a rapid settling of the solid impurities. By means of the two valves at the bottom, the sludge is discharged into the trucks, W, and can be filter-pressed before being sent away. The clear liquid issuing out of F is used for heating-up the fresh sewage in A, as before described. The necessary heat is supplied to this apparatus by direct (wet) steam, through a 1¼-inch steam-pipe, *v*, just above the bottom of E.

This apparatus is capable of treating 65 tons of sewage matter per 24 hours. It is easy to clean, as all the overflow-pipes are arranged in outside annexes, X X, which are accessible by taking off the flanges.

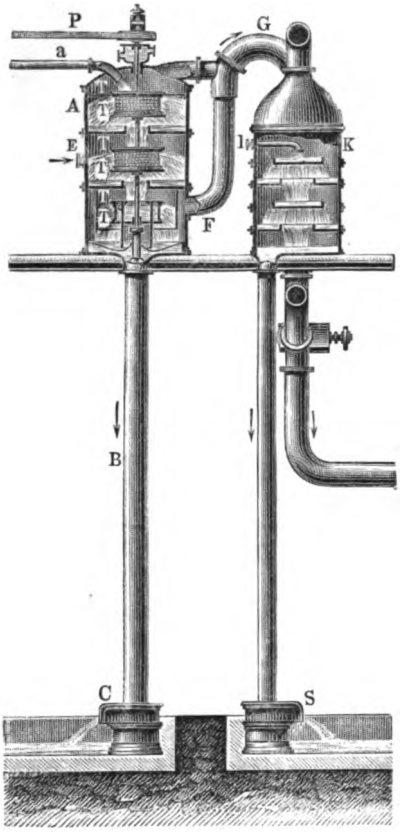
One of these apparatus has been at work since 1881 at La Tresne, near Bordeaux, and several others seem to be working satisfactorily in France.

Lencauchez's Apparatus

works under diminished pressure, and consists of two quite distinct parts. The one shown in figs. 173 and 174 is called the "barometric chamber," and serves for expelling the volatile ammonium salts. It is a wrought-iron cylinder, A, 7 feet 4 inches diameter, and 11 feet 4 inches high, fixed on the top of an iron column, B, of a height of 33 feet, at the bottom of which a siphon-pipe carries off the spent liquor into the tank C. In this "barometric chamber" a good vacuum can be kept up by an air-pump which continually aspirates the gases and vapours given off by the sewage; this gaseous mixture is, as usual, absorbed in sulphuric acid, whilst the spent liquor runs off at the bottom of the column B, in which the liquid rises equal to the atmospheric pressure. The chamber A is divided

into three compartments, in which as many small turbines, T, T, T, set in motion by the pulley P, convert the sewage which arrives in

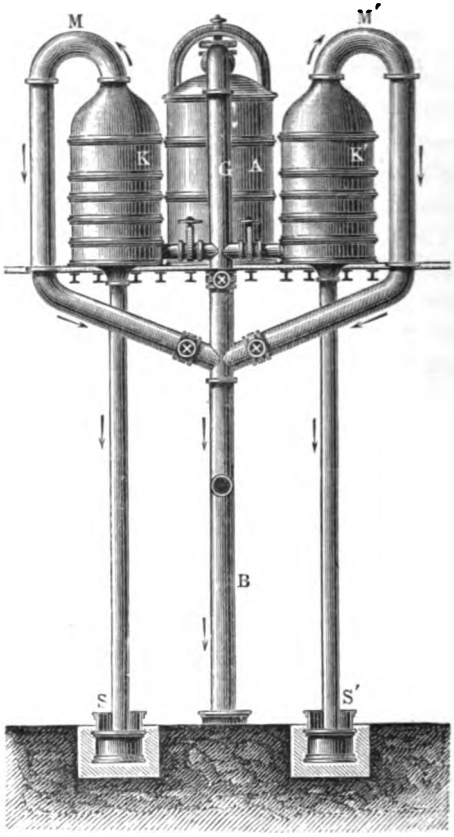
Fig. 173.



the pipe *a*, three times over, into a fine spray, which greatly facilitates the escape of the volatile ammonium salts. The liquor is heated by means of the exhaust-steam of the engine, through the pipe E. The steam and vapours, issuing through F and G, pass alternately through one of two saturators, K K′, arranged on a similar principle as the chamber A. These are 6 feet wide, and are provided with horizontal diaphragms for dividing the acid into a spray. The quantity of acid and the time it stays in the saturator

must be so regulated that all the ammonia is absorbed and yet the acid is saturated. The solution of ammonium sulphate runs down

Fig. 174.

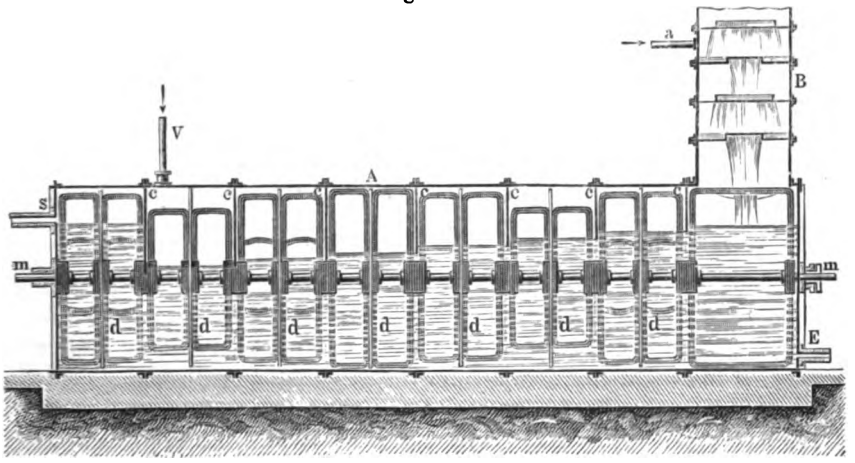


the column and through the siphon, S, into a crystallizing-vessel. The pipes M or M′ carry off the noxious gases, which are aspirated by the air-pumps, freed from moisture by cooling down, and burned in the usual manner. The condensed liquid, which contains a little ammonium salt, is sent into the apparatus to be described next.

Fig. 175 shows that part of Lencauchez's apparatus which deals with the "fixed" ammonium salts. It is a horizontal cylinder,

10 feet in diameter and 33 feet long, provided with a longitudinal shaft and agitating-paddles for mixing the liquor with milk-of-lime.

Fig. 175.



Between the paddles there are seven disks for diminishing the speed of transit of the vapours. These seven partitions, *c c c*, divide the cylinder into eight chambers of equal size. The first partition from the left reaches down to the centre of the cylinder; the following ones are each 6 inches smaller than those preceding. A tube, V, enters into the second chamber, and injects into it the exhaust steam from one or several steam-engines; the last chamber is surmounted by a cast-iron rectifying-column, B. The first plates of this column have simple holes, without covering-cups, so as not to be stopped up by solid matter projected from below; its upper portion is connected with two reflux-worms and a receiver for crude concentrated ammoniacal liquor. For making sulphate the worms are not cooled so much, and the vapours from them are conveyed into a sulphuric-acid saturator.

Into this apparatus the liquor, deprived in the "barometric chamber" of its volatile ammonium salts, is introduced through *a*, at the third chamber of the column B; it descends in thin jets, and gets into the horizontal cylinder, where it is mixed with milk-of-lime. The ammonia of the fixed salt is thus set free, and comes off gradually in the different chambers; it passes on successively from one to the other by bubbling through a mixture of liquor and lime,

each time traversing a layer 6 inches deep. At last, after about half an hour, the liquor arrives totally spent at the other side of the cylinder, and runs to waste by the siphon-tube S.

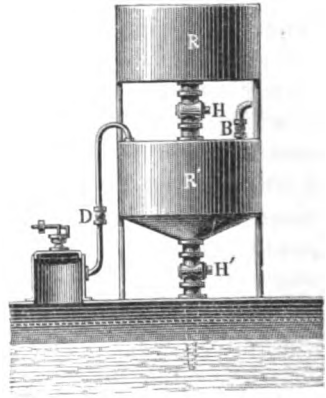
This apparatus is very ingeniously constructed, but seems too complicated, and has not made its way outside of France. It is doubtful whether the very much simpler means employed in England and Germany do not fulfil the aim in view quite as well.

Recent Proposals for improving the Manufacture of Ammonium Sulphate (partly referring also to Liquor Ammoniæ).

Rousseau (Fr. P. Aug. 18, 1880) recommends that in rectifying ammonia by dephlegmation the water be kept at a temperature of from 60° to 70° C.; below this, *e. g.* at 55°, the liquor begins to take up ammonia from the gases passing through.

Hegener (G. P. 11669) prevents the escape of ammonia in charging with milk-of-lime by means of two tanks placed above the still. In the upper one (R, fig. 176) the lime is slaked, and the milk-of-lime is let down into the lower one, R′, by the cock H. During this the ammoniacal gases in R are conveyed to a special receiver by a pipe proceeding from the air-cock B. When the milk-of-lime is to be run into the still, the cocks H and B are closed, but H′ and the steam-cock D are opened.

Fig. 176.



An apparatus patented by the Société anonyme des produits chimiques du Sud-Ouest (G. P. 13429) does not seem to offer any special advantages over those already described.—That of Rube, Engelcke, and Krause (G. P. 15570) consists of a column formed of a number of funnels superposed over one another, into which ammoniacal liquor and milk-of-lime are introduced by separate siphon-pipes.—G. Wunder (G. P. 17411) employs the old principle of two boilers, one for the volatile and one for the fixed ammonia, the latter being heated by the steam coming from the

former, which itself is heated by a fire.—J. Gareis (G. P. 21707, B. P. 3164, 1882) employs a combination of four vessels, so arranged that the one filled with milk-of-lime is not, like the lowest, heated by a direct fire, but by the steam coming from the latter, just as is done (in a more perfect way) in the Grüneberg stills, p. 639.—F. Gerold and M. Vacherot (G. P. 21821) patent a travelling apparatus for working gas-liquor, consisting of a simple cylindrical boiler, with an inside fire-tube, like a Cornish boiler, resting on a railway-truck. (This form of boiler is quite unsuited for distilling gas-water, especially with lime, as proposed by the inventors.)—C. H. Schneider's apparatus (G. P. 21252) is a two-boiler still with dephlegmator, without any essential difference in principle from the ordinary apparatus.—The same holds good of the apparatus of C. Brison (B. P. 11449, 1884), which contains a directly fired retort of peculiar shape.—C. Hills (B. P. 5874, 1884) heats the gas-liquor as it descends in a scrubber, the heat being applied to the lower part of the scrubber. By this means the temperature of the descending stream of gas-liquor is gradually raised, and most of the sulphuretted hydrogen and carbonic anhydride, and some ammonia, are expelled, the latter being absorbed by the cool gas-liquor in the upper part of the scrubber, whilst the H_2S and CO_2 pass away from the scrubber.—A. Dempster (B. P. 3220, 1886) claims the following improvements:—(1) heating the sulphuric acid in the saturator and the ammoniacal liquor in the feed-tank by means of the noxious gases generated in the saturator; (2) constructing the still with a decomposing-chamber under the fire-box for getting off the fixed ammonia, the milk-of-lime in this chamber being agitated by ammoniacal gases instead of steam, as is usual; (3) providing the still with a diaphragm in order to concentrate the ammoniacal gases; (4) drawing air along with the noxious gases through the purifier; (5) employing a vertical rod for actuating several valves simultaneously.—Heinrich Hirzel, of Plagwitz, near Leipzig, supplies ammonia-stills of a special construction, especially for making pure concentrated liquor ammoniæ.—N. M. Henderson (B. P. 15836, 1885) proposes some modification of the ordinary rectifying-column.

Pfannenschmidt (Journ. f. Gasbeleuchtung, 1884, p. 266) recommends the following way of disposing of gas-liquor, together with the spent oxide, at small works where it does not pay to

put up any apparatus:—The spent oxide is spread out under an open shed in a thickness of six or eight inches, and is drenched with as much liquor as it will take up. On the top of this another layer of six or eight inches is spread out, and is again drenched with gas-liquor, and this is continued several times; but the top layer is left in the dry state. After a few days the heap is turned over several times till dry, and is then capable of receiving more liquor. This work must, of course, be done in dry and warm weather and in a place sheltered from rain. The ammonium sulphide of gas-liquor with the iron oxides forms ferrous sulphide, and from this the oxygen of the iron forms ferrous sulphate. This again acts upon the ammonium carbonate and sulphide, ammonium sulphate being formed, and ferric hydroxide, along with FeS, being regenerated, which will again take up atmospheric oxygen and form more sulphate, capable of fixing ammonia. In this way the oxide can be charged with as much as 32 per cent. ammonium sulphate, and this can be made to bear a good deal of transit expenses. [It is evident that much ammonia will be lost in this way, and some nuisance produced. This process will be practicable only in exceptional cases.]

Commercial Sulphate of Ammonia.

The properties of pure ammonium sulphate have been described, p. 591. The commercial salt, when made with sulphuric acid free from arsenic and iron, should be white, or at least light grey. The salt formerly made by direct saturation of gas-liquor with sulphuric acid was, of course, dark grey or brown; and even that now made by distilling ammonia into sulphuric acid has a dark colour, unless precautions are taken against this by the mode of saturating the liquor (p. 602). It must also be noted that the sulphate made in the more perfect apparatus, as those of Grüneberg, Feldmann, and others, is of itself much less liable to be coloured, because the tarry impurities are mostly condensed in the dephlegmating columns. But even then the sulphate may, after some time, assume a yellow colour from iron salts gradually accumulating in the saturator; this is avoided by cleaning the latter out from time to time. Sulphide of arsenic also causes a yellow colour, and for this reason the English manufacturers regularly employ brimstone acid; but even in Germany, where pyrites acid is exclusively used, the sul-

phate is not usually yellow, partly because sulphuric acid made from pretty pure pyrites is generally employed, partly because the arsenious sulphide can be skimmed off during saturation, sometimes with special additions (pp. 444, 603).

Sulphate coloured bluish (evidently by Prussian blue) has also been observed*. This impurity can be avoided by not employing any iron pipes for conducting the ammoniacal vapours.

The ammonium sulphate, as it comes from the saturators, is often merely drained and sold in the moist state; in this case it will be very perceptibly acid. This can be avoided by carefully washing it, with very little water, on the drainer, but more easily by employing a centrifugal machine lined with lead, in which also the washing can be performed.

The drying of the salts, if necessary, can be performed in stoves, heated by the waste heat of some flue or by exhaust steam from an engine, or on open floors or plates heated from below.

Ammonium sulphate is always sold according to its percentage of nitrogen or ammonia. Chemically pure salt would test 21·21 per cent. N, or 25·75 per cent. NH_3, and even commercial salt sometimes tests 24 or 25 per cent. NH_3. The analytical processes serving to ascertain the percentage of ammonia will be mentioned hereafter.

In the English trade the strength usually stipulated for between buyer and seller is 23 per cent NH_3. As the manufacturers found that they could get up to 25½ per cent., they brought this down to 23 per cent. by adding common salt or sulphate of soda; but some buyers object to this in the sale-note. (Watson Smith, priv. comm.)

In England it is usual to quote the strength of ammonium sulphate as percentage of ammonia, in Germany as percentage of nitrogen. The table on p. 666 will help in quickly reducing these terms to one another.

A most objectionable impurity in ammonium sulphate is *ammonium sulphocyanide*. This is scarcely found in such salt as is obtained by distilling gas-liquor with lime and absorbing the gas in sulphuric acid; but it may occur in the salt obtained by direct saturation of gas-liquor with acid, and it is regularly found in the salt which is made by washing spent oxide of iron from purifiers, and simply evaporating the washings. The latter product contains

* Chemiker-Zeitung, 1866, Repertor. p. 282.

Table for comparing the percentage of Nitrogen and that of Ammonia.

N.	NH_3	N.	NH_3.	N.	NH_3.	N.	NH_3.
0·1	0·12	0·9	1·09	8	9·71	16	19·43
0·2	0·24	1	1·21	9	10·93	17	20·64
0·3	0·36	2	2·43	10	12·14	18	21·85
0·4	0·49	3	3·64	11	13·35	19	23·07
0·5	0·61	4	4·86	12	14·57	20	24·29
0·6	0·73	5	6·07	13	15·78	21	25·40
0·7	0·85	6	7·29	14	17·00	...	...
0·8	0·97	7	8·50	15	18·21	...	...

frequently 25, sometimes even up to 91 per cent. of sulphocyanide *. Since this salt is very injurious to vegetation †, and lessens the value of ammonium sulphate, or even makes it quite unsuitable for manuring-purposes, such solutions from spent oxide ought never to be utilized by direct evaporation, but should be distilled with lime; from the residue calcium sulphocyanide may be extracted, and may be worked up into sulphocyanides, which have now become articles of commerce.—The detection of sulphocyanide in commercial sulphate is very easy, by the well-known red colour which it gives with iron per-salts; even its quantitative estimation by a colorimetrical process might be founded upon this reaction, but it is best done gravimetrically by precipitation as cuprous sulphocyanide, as described p. 577.

Most of the ammonium sulphate is employed as manure; for the cultivation of beetroot especially it cannot be replaced by the cheaper nitrogen of nitrate of soda; hence the very large importation of this salt into Germany, comp. p. 544. The sulphate also serves for preparing the other ammonium salts, and

* Esilman and Bell, Chem. News, xxxii. pp. 124, 197.

† The damage done to plant-growth by ammonium sulphocyanide (thiocyanate), which was considered a matter of notoriety, has been represented as slight by Mr. Märker (Biedermann's 'Centralblatt für Agrikulturchemie,' 1883, p. 494). But the researches of P. Wagner (ibid. 1873, p. 336), of C. Schumann (ibid. 1882, p. 332), and of C. Böhmer (Wagner-Fischer's Jahresb. d. chem. Technol. 1884, p. 324), on the contrary, fully prove the injurious action of the sulphocyanides on plants.

sometimes for liquor ammoniæ, and for making ammonia-alum. Considerable quantities of sulphate are also used in the manufacture of ammonia-soda; the quantity annually consumed for this object probably amounts at present to about 10,000 tons. A 10-per-cent. solution of ammonium sulphate is employed to render tissues, papers, &c. non-inflammable.

The amount of ammonium sulphate at present manufactured in the United Kingdom is estimated at about 100,000 tons per annum. According to the 'Chemical Trade Journal,' 1887, p. 4, there was made in 1885:—in Scotland and Ireland 18,274 tons in oil and iron works, 8855 tons in gas-liquor works; in the north of England 3000 tons; in Cheshire, North Wales, Lancashire (West), 3948 tons; East Lancashire and Yorkshire 16,000 tons; South-west of England 3420 tons; London and South-east 33,000 tons. The production in winter months (October to March) is twice as much as in the summer months. Most of it is exported; the amount of importation into Germany has been mentioned, p. 544, where it is also stated that about 10,000 tons per annum are manufactured in that country itself. France produces about 12,500 tons; Holland and Belgium about 3000 tons.

From a private source, I have received the following notes on the ammonia industry in the United States of America. Gas-liquor is worked up only at the larger gas-works and a few commercial centres. It is generally only 2-ounce liquor, and is treated in very primitive apparatus, ordinary horizontal boilers, without any of the improvements introduced in Europe. The yield of sulphate may be estimated at 20 lb. per ton of coal, and the total quantity manufactured in the United States at 11,000 tons per annum.

Manufacture of Liquor Ammoniæ.

Liquor ammoniæ is a more or less pure and more or less concentrated solution of caustic ammonia in water. Beside ammonia it frequently contains compound organic bases and other tarry products, which impart to it a disagreeable smell, and sometimes also a yellow or brownish colour. This yellow (amber) colour is often not present in the freshly prepared liquor, but is developed from the empyreumatic substances in course of time, especially under the influence of sunlight. The liquor ammoniæ

derived from sewage, directly or indirectly, contains hardly any of these impurities, while that derived from gas-liquor is sometimes very much contaminated with them.

Formerly liquor ammoniæ was prepared by distilling sal ammoniac with slaked lime; and for analytical purposes this is still done sometimes, but even here only exceptionally, since the sulphate is very much cheaper than the hydrochloride. When employing sulphate, it is usual to carry on the operation in a cast-iron still provided with an agitator, to prevent a crust of calcium sulphate from impeding the further reaction of the lime upon the ammonium salt. Even from sulphate very little caustic ammonia is made now-a-days, since it is now easy to make it directly from gas-liquor, in one or two distillations.

Although it is not at all intended as a process for manufacturing liquor ammoniæ, but, on the contrary, as a step in the manufacture of ammonia-soda by a new process, we will briefly mention the invention of E. Carey and F. Hurter (G. P. 30198, of 1884). They mix ammonium sulphate with its equivalent of sodium sulphate, and heat the mixture in the presence of steam to 350–370° C. The ammonium sulphate is then decomposed; its sulphuric acid with the sodium sulphate forms sodium bisulphate, whilst its ammonia is set free, and is employed, along with carbon dioxide, for converting another portion of sodium sulphate into carbonate. The sodium bisulphate formed in the above process is heated with common salt, and yields hydrochloric acid and neutral sulphate. This very ingenious and promising process had up to the date of writing this not yet entered into real manufacturing practice.

When making liquor ammoniæ directly from gas-liquor or any other ammoniacal liquor containing principally ammonium carbonate and sulphide, sufficient lime must be added from the outset to retain the carbon dioxide and hydrogen sulphide. This may entail much trouble in consequence of crusts of lime forming on the walls of the stills, which must be overcome by special means. When white and pure caustic ammonia is required, the empyreumatic substances must be retained or destroyed. The most usual means for doing this is filtering the vapours through recently ignited wood-charcoal. Some recommend, as more convenient, passing the vapours through a fatty oil which retains the tarry substances, and can be again partially freed from them by

heating; or else redistilling the liquor with potassium permanganate. But these means are rarely employed, as they are in reality more troublesome and expensive than wood-charcoal, which can be made fit to be used over and over again by reigniting in close vessels, and when quite inactive for filtering the vapours is still useful as fuel.

Watson Smith * advises in any case, even when liquor ammoniæ is the principal product, making along with it a little sulphate, because the gas which first and somewhat tempestuously escapes in the distillation carries along with it some tarry matters and hence is best not employed for making liquor ammoniæ. This of course cannot be observed in the continuously acting apparatus to be described below; but even then mostly only crude strong ammoniacal liquor is at first obtained, from which liquor ammoniæ is prepared by distilling into pure water. In order to carry off separately the first evolved portion of ammoniacal gas, the gas-delivery pipe of the ammonia-still is provided with two branches, each of them to be shut off by a stop-cock, or by a short piece of 2-inch india-rubber pipe with a screw clamp, in order to direct the vapours either into the ordinary saturating-vessel filled with sulphuric acid, or into a worm for condensing crude liquor ammoniæ. The latter is collected in large iron tanks, from which the vapours pass first through a barrel half filled with water, or preferably, to avoid pressure, through a lead worm, serving as a reflux condenser, in which the vapours ascend and are met by water trickling down from a funnel, to condense the last traces of ammonia. (No doubt a small coke-scrubber, fed with water, or preferably with sulphuric acid, would act even more thoroughly.)

From this crude liquor (or any other crude concentrated ammoniacal liquor) pure liquor ammoniæ is prepared by very many descriptions of apparatus. A very simple form of this, which was in operation at a Manchester works some years ago, is shown in fig. 177. The liquor is put into a still *a*, 8 feet long and 4 feet in diameter, heated by a fire, which is kept away from the bottom of the still by an arch, and only circulates round the sides. For each charge of 600 gallons, containing 3½ to 4 per cent. ammonia, 2 cwt. of quicklime, previously slaked to a thick paste, is added, and a strong fire is made. The gases escape through a 2-inch pipe

* Private communication.

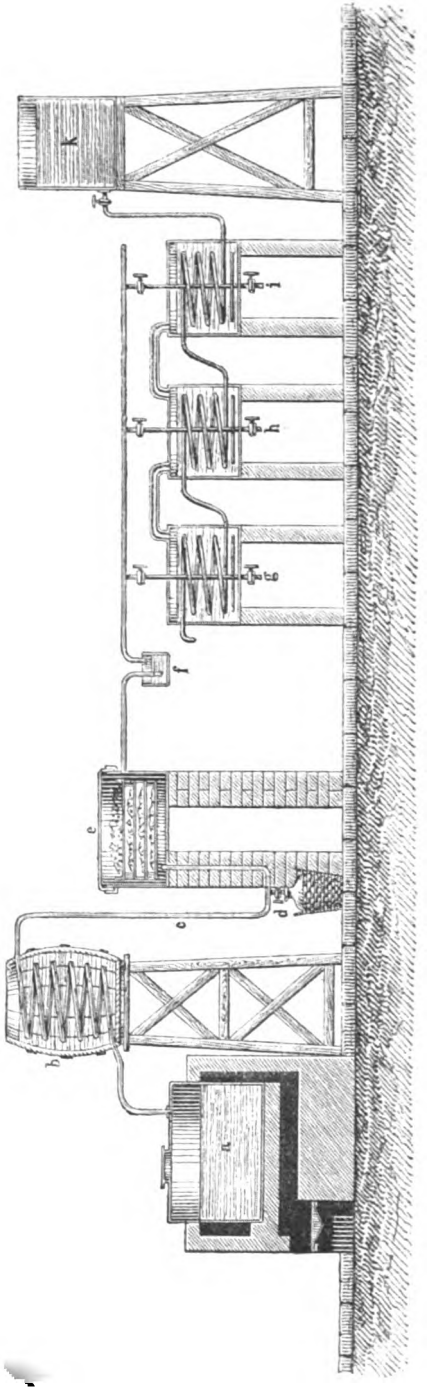


Fig. 177.

into the lead worm *b* (cooled outside by water), in which the aqueous vapour is condensed and flows back. In the descending branch *c* a little water is condensed and collects in the carboys *d*. The nearly dry gas is treated in the purifier *e* (6 feet long and 4½ feet wide) with slaked lime, to remove hydrogen sulphide, tar, &c. The top of the purifier is luted with lime-putty, and is screwed down tightly; its contents must be renewed two or three times a month. From this the gas passes in a 1-inch pipe through a small washing-arrangement *f*, and then, by means of india-rubber joints provided with screw-clamps, at will into one of the three absorbers, *g*, *h*, *i*, made of iron lined with lead, 3½ feet square and 3 feet high, and provided with gauge-glasses. These vessels are charged with pure water; the gas issues into them from perforated rings of lead tubing lying at the bottom. The vessels are connected by gas-pipes; they also have an air-vent each; but of course this is only opened in the last one of the series. The contents of *g*, *h*, *i*, are cooled by water, which, coming from the tank *k*, is passed through all the absorbers by means of worms. After the liquor has become sufficiently strong, it is drawn off by taps into carboys, ready for sale. It should be clear, free from any greasy matter, and of sp. gr. 0·905, or at most 0·914. No traces of sulphides, indicated by lead acetate or sodium nitro-cyanide, should be present. (This description may serve to show how an apparatus can be constructed in a cheap and simple manner; but it lacks some of the perfections of those more modern appliances.)

Apparatus of Elvers and Pack.

Fig. 178 is a sketch of this "two-boiler" apparatus for making liquor ammoniæ direct from gas-liquor. We have not reproduced the original sketch, which is somewhat difficult to understand, but placed the parts separately alongside one another, to make the principle clearer. For the same reason all supports, carrying-walls, &c. are left out. A and A′ are cylindrical iron boilers, A′ being placed sideways and above A, which alone is directly heated by the fire. A is surmounted by a dome, to which are attached an air-valve *v*, for avoiding a collapse of the still by the atmospheric pressure on cooling, and the gas-delivery pipe *a*. The latter is carried first up, then downwards, and enters

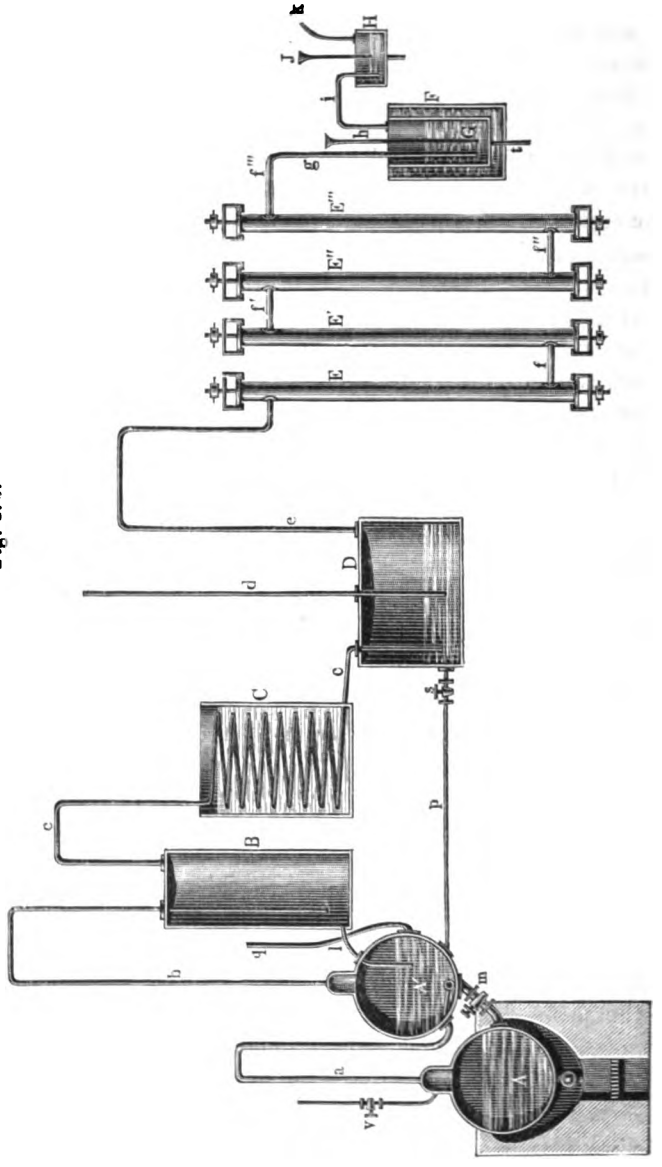


Fig. 178.

A′ near the bottom, continuing into a pipe running all along the bottom and perforated with many holes, through which the vapours from A get into A′. The liquid in A′ can be run into A by means of the wide pipe and valve *m*, which can be cleaned from deposit by means of a suitable contrivance. The vapours arising in A′ first ascend in *b*, then descend into the vessel B to within 12 inches of its bottom; the liquid condensed in B runs through *l* into A′ below the level of the liquid there. From B the vapours enter the worm C, and through *c* the closed box D. From this the condensed liquid can be run back into A′ by the tap *s* and the pipe *p*. D carries a safety-tube *d*, and a pipe *e* for taking away the uncondensed gases. These, now mostly freed from moisture, pass into the four cast-iron pipes E E′ E″ E‴, connected alternately at top and bottom by the pipes *f f′ f″*; they are open at both ends, and closed by plates tightly screwed down. From E‴ the gas travels through *f‴* and *g* into the leaden absorbing-vessel G, placed in a cold-water tank F; here also a safety-pipe *h* and a discharge-pipe *t* are provided. The residual gas gets through *i* into a small absorbing-vessel H, with safety-pipe J; and *k* carries the incondensable gases into the outer air.

First the still A′ is charged by the pipe *q* with about 1000 litres of gas-liquor, contained in a higher store-tank; and this is at once mixed with a sufficient quantity of lime through a special aperture. The value *m* is opened; the condensers C and F are charged with cold water, the pipes E E′ E″ E‴ with freshly ignited wood-charcoal in pieces the size of a walnut; and the covers are screwed down. G is charged with 60 or 65 litres of water, H with ½ litre. When the liquor mixed with lime has flowed from A′ through *m* into A, *m* is closed and the fire is lighted. The fire-gases travel along one side of the boiler, return along the other, and then go to the chimney. When the contents of A begin to boil, first the air is expelled and passes in bubbles through the water in G and H; A′ and the pipes are filled with vapours and get heated. Gas-liquor is now run through *q* into A′; by the cooling thus produced the liquor in D is sucked back into A′ through *c* and *b*, and air enters at *d*. When 1000 litres of gas-liquor have run into A′, milk-of-lime is again added and well mixed, whereupon the fire is started again. The ammoniacal vapours from A escape through *a* into the liquid in A′, traverse this from the many small holes of the pipes, and give

off part of their ammonia to it. A portion of the steam is condensed in B, the water running back into A′ through *l*, along with the volatilized salts. From B the vapours pass into C, where most of the water, together with a portion of the ammonia, is condensed. The condensing liquid serves for washing the ammoniacal vapours, and especially for retaining the salts carried away with them. The uncondensed vapours pass through *e* into the charcoal-purifiers, which absorb the impurities mixed with the ammonia-gas. In G the pure ammonia-gas is condensed by cold water, and liquor ammoniæ is obtained. The last remnant of the ammonia is absorbed in H, by sulphuric acid; the incondensable gases escape through *k*. When the still A is worked off, the residue is discharged, and it is recharged from A′. The liquor now re-aspirated from D into A clears the worm C &c. from any deposit. If in G and H ordinary water, not distilled, has been employed for absorbing the ammonia, the precipitate of calcium, aluminium, and magnesium salts formed must be allowed to settle, in order to obtain a clear, marketable product. Each operation takes 4 or 5 hours; and from 1000 litres of gas-liquor of 3° Baumé is obtained 100 to 110 kilogrammes of liquor ammoniæ of 22° Baumé (=sp. grav. 0·924).

We have pointed out more than once the drawbacks attaching to the direct contact of fire with the mixture of liquor and lime in the first of the boilers. This direct contact is avoided in the Grüneberg stills, fig. 163, p. 640; but even these are not adapted to using sufficient lime for retaining all the carbonic acid and hydrogen sulphide. Altogether it seems preferable in every way to use for this purpose stills heated by direct steam. That of Grüneberg and Blum, fig. 167, p. 647, can be adapted for the production of liquor ammoniæ in the way represented in the sketches figs. 179 and 180. A is the ammonia-still; B, the economizer for condensing watery vapour and at the same time heating up the fresh liquor; C C′, lime vessels through which the vapours are made to pass; E E′, lime-washers following upon these, to retain the last traces of CO_2 and H_2S; D, a cooler constructed like that shown in fig. 166, p. 640, to condense as much water as possible out of the gases; F F_1 F_2 F_3, charcoal-filters; G G_1, boxes for absorbing the purified ammonia-gas in water. The gases pass alternately into one or the other of the lime vessels C C′ and lime-washers E E′. The partially saturated lime from these is used in

the first still (which for this purpose, if direct firing cannot be avoided, is replaced by a horizontal boiler fitted with a longitudinal agitating-shaft). The drying and cooling of the gases in the

Fig. 179.

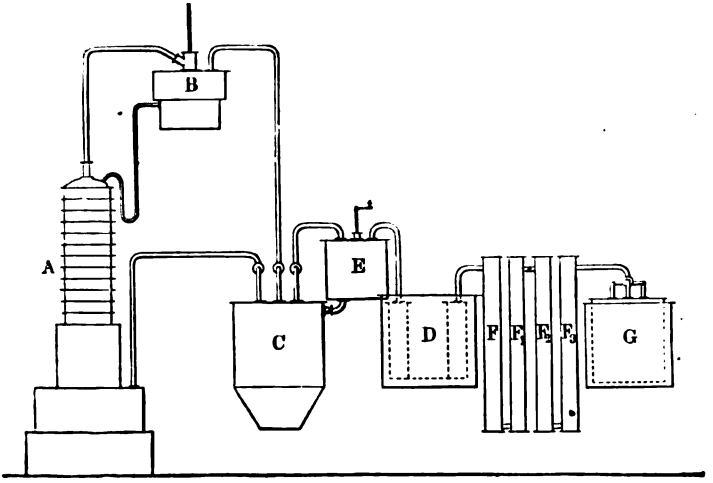
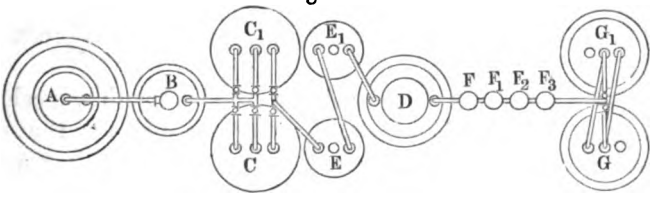


Fig. 180.



cooler D (which is best supplemented by an empty iron cylinder, through which the gases pass before entering D) is indispensable to secure a proper action of the charcoal-filters. These must of course be of sufficient number and size to effect their purpose; in one instance which I witnessed there were eight cast-iron pipes, each 1 foot wide and 3 feet high. The filtered gases are conveyed through both the absorbing-boxes G G_1 in this way:—the box which has been the second in one operation and only contains weak liquor ammoniæ is made to act as first absorber in the next operation, when its contents are brought up to full strength; while the other box, which had been refilled with fresh water, now acts as second absorber, and only retains the ammonia coming over

from the first box. These absorbers are cooled on the outside by a water jacket, and inside by a cold-water worm.

The cooling in every kind of apparatus for liquor ammoniæ must be very good, and for the strongest liquor even ice must be employed.

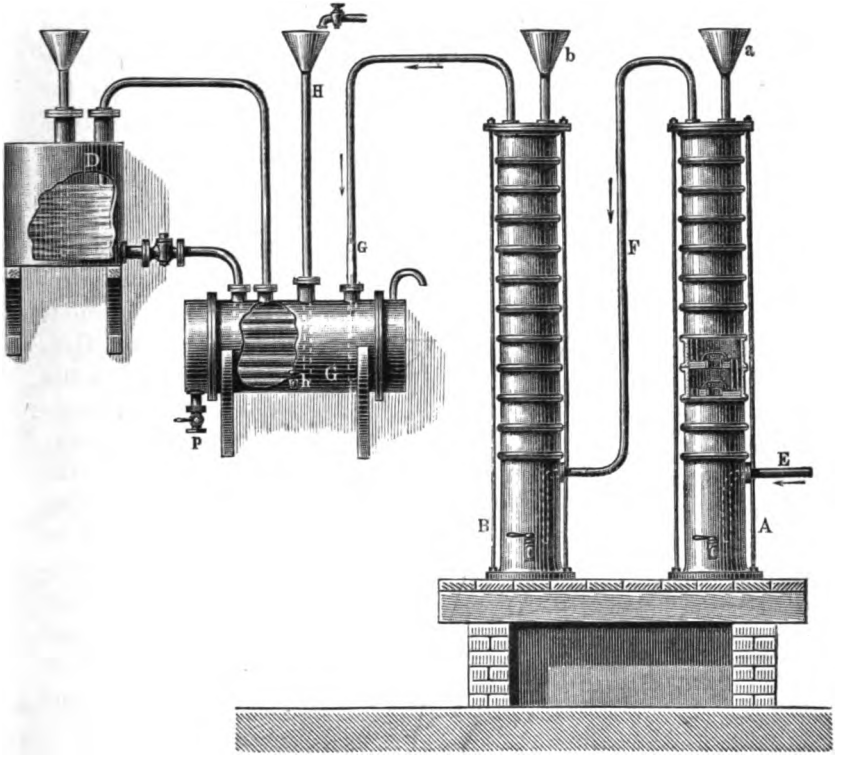
Feldmann (B. P. 11711, 1884) operates in quite a different way. He objects to the employment of lime-washers &c. after distillation; his principle is, employing a sufficiency of lime *before* distillation, and separating the precipitate formed after some time by means of a filter-press. In lieu of the greenish, slimy residues otherwise produced, which are very difficult to dispose of, there are obtained, by means of a filter-press, solid cakes, from which the last portions of ammonia are recovered by a washing arrangement and by excluding the air during the operation. The filtered liquor is now distilled in a column, and the distillate can be brought up to 25 per cent. NH_3, but is still an impure liquor, since the ammonium sulphide is not decomposed by the cold treatment with lime. It is, however, completely decomposed by re-distilling with an excess of lime, say, twice the theoretical quantity. As the quantity of liquor is now very small, and the ammonium sulphide on the average is only one twentieth of the total ammonia, there is no difficulty whatever in that re-distillation, especially as the calcium sulphhydrate is produced in a liquid form.

P. Mallet recommends his column provided with a mechanical agitator (p. 653) as being particularly adapted for the manufacture of caustic ammonia, where a large excess of lime must be employed.

We have also seen that the old apparatus of A. Mallet can be used for making liquor ammoniæ, but only the yellow article. In order to make white liquor, he employs the apparatus shown in fig. 181. Here A is a cast-iron column, 1 foot 6 inches wide, formed of 14 chambers containing a solution of caustic soda, introduced by the funnel *a*. B is a similar column containing a vegetable fatty oil, or heavy mineral oil for retaining the empyreumatic substances (p. 668); G, a wrought-iron tubular saturator, through whose tubes a current of cold water is constantly passing, to cool the liquor during the condensation of the ammonia; D, a cast-iron safety vessel in which the gas escaping the action of water in the saturator D is retained. The gas coming from the ammonia-still (where plenty of lime has been employed) enters at E into the

column A and there parts with most of its impurities, and is completely causticised; in the column B most of the organic alkaloids and empyreumatic substances are retained by the oil; the purified gas meets with cold water in the saturator G; and when the solution is strong enough, it is run off by the tap *p*. The liquor contained in

Fig. 181.



D is now run into G; D is refilled with pure water, and the operation is started again. The liquor ammoniæ thus made keeps white even in the sunlight; but it still contains traces of foreign products, as is proved by its being more or less coloured brown by nitric acids. Liquor which is to stand this test as well must be made from sewage liquors.

Ammonia-Stills used in the Manufacture of Ammonia-Soda Ash.

The task of making soda ash by the ammonia process has only

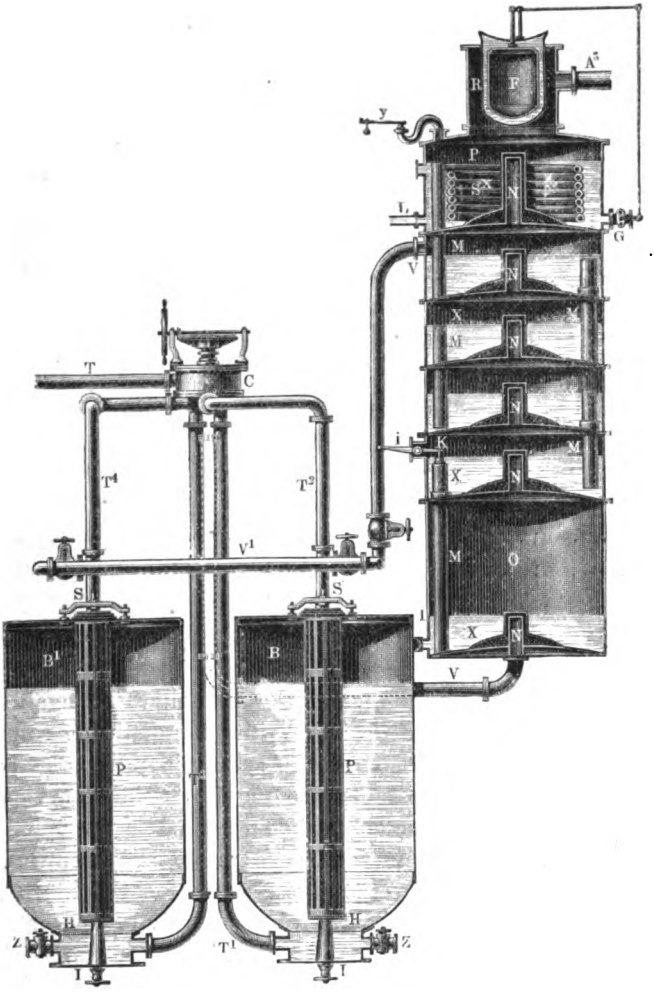
become possible since apparatus have been constructed capable of recovering nearly the whole of the ammonia, within a very small fraction indeed, from the enormous quantities of ammonium chloride formed in that manufacture. It is computed that ammonia equal to about 10,000 tons of sulphate per annum is wasted in making soda; but that means that a quantity of ammonia 15 or 20 times as much as the above has to be distilled over and over again from the ammonium-chloride liquors. Hence the scale on which this distillation is carried on far exceeds that of ordinary ammonia-works, which manufacture ammonium compounds for commerce, and the apparatus employed in the ammonia-soda works is on a corresponding scale, that is, rather too complicated and costly for other uses.

In principle the task is very nearly the same as that which we have treated of in the preceding pages. The mother-liquors, separated from the sodium bicarbonate, contain both "volatile" and "fixed" ammonia; but the latter here prevails to an enormous extent, so that very much lime must be used in the distillation. On the other hand, since that manufacture requires the ammonia in the state of carbonate, and since no sulphide is in question here (apart from the relatively insignificant quantity introduced by any fresh gas-liquor brought into the works for making up losses), the operation must be carried out in the same manner as in distilling gas-liquor for sulphate; that is, the volatile ammonia must be driven off first, and only subsequently the fixed ammonia is decomposed by lime. But since the latter here largely prevails over the former, the apparatus which has been found excellent for manufacturing ammonium sulphate would not equally answer in this case, as it is calculated for liquors containing only about one fifth of the ammonia in the fixed state.

It follows from this that every one of the extremely numerous attempts at practically carrying out the ammonia-soda process involves the construction of an ammonia-still specially adapted to the above requirements. It is entirely out of the question to enter into all these constructions in this work; we will, however, as one of the very best examples of how that task has been solved, give a description of the ammonia-still constructed by the most successful of inventors in that line, Ernest Solvay, as contained in his patent No. 1904, 1876. It is worked entirely by the exhaust-steam from the blowing-engines employed in the process.

Figs. 182 and 183 are a section and plan of the apparatus. The liquor filtering from the bicarbonate passes first through the column A for distillation without lime, and then through the four stills B to B^3 for distilling with lime. The stills B, B', B^2, B^3 com-

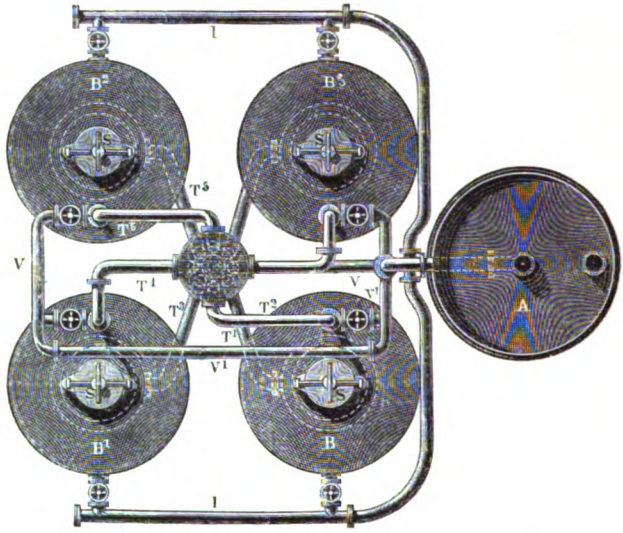
Fig. 182.



municate with each other by a distributer C, similar to those used in gas-works, which permits any boiler to be isolated without inter-

rupting the distillation in the others. As a rule, one still is stopped for discharging and charging while the other three are working. The exhaust-steam from the engines passes through the pipe T

Fig. 183.

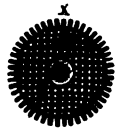


into the distributer C, and from this by T^1 to the longest-working still B; from here it comes out by T^2, again into the distributer C, and passes through T^3 into the second still B^1. Similarly it passes into the last-filled still B^2; so that fresh steam always enters that still the liquor of which has only to be deprived of the last traces of NH_3. When the steam leaves the last still B^2, it again enters the distributer and passes through V into the distilling column A, where it causes the expulsion of the ammonia present as such or as carbonate. In this column the mother-liquor from the bicarbonate running down condenses the steam, while the NH_3 passes on, and the mother-liquor receives a preliminary heating. The last cooling is effected in the upper part of the column by the refrigerator P, so that from the pipe A^3 only gaseous ammonia with some ammonium carbonate escapes, but no steam—which is very important, since the gas from here passes direct into the "dissolvers" for brine, and this must not be diluted with water. Within the refrigerator P is the cooling-coil S, filled with liquid to be distilled, which thus receives a first heating. On the top is

a regulator, consisting of a float F in a vessel R, filled with a little water.

This water is more or less heated by the gas passing through; the warmer it is, the more the float descends, and it ultimately opens a cock G, which admits fresh liquor into the coil—or in the same way as the admission of steam into the distilling-apparatus is regulated. From the coil the liquor runs out by L into the interior of the distilling column, and from this by *l* into that one of the lower stills which has just been emptied and freshly charged with lime. When just as much liquor has collected in the lower part O of the column A as suffices for filling one of the stills, which can be seen by means of a gauge-glass, the valve K is closed by the lever *i*, and a further descent of liquor into O prevented. Otherwise the liquor in the column always runs off by the overflow M, whilst the central pipes N convey the ammonia gas and the steam. The convex small bottoms X, separately drawn in fig. 184, serve for distributing the steam in the liquid; they are perforated with many conical holes, and are nicked all round. *y* is a safety-valve at the end of a swan-neck pipe filled with water or petroleum, which prevents the ammonia from corroding the metal of the valve.

Fig. 184.



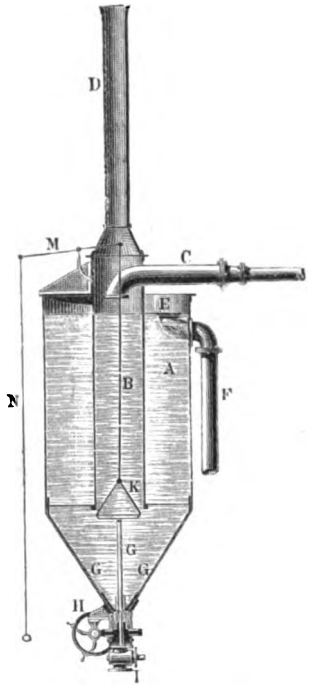
In the stills B to B^3 the ammonium chloride must be decomposed by lime. For this quicklime, straight from the kilns, is put through the doors S into the central (or lateral) cages P, which retain the unburnt pieces, stones, &c. The NH_4Cl liquor ascending in the still B slakes the lime; and the heat evolved in this assists in the distillation: this can never take place with such violence as to cause any danger, since in this case the evolved gas and steam would force back the liquor and not permit it to enter into the cage. Thus the heat of the slaking lime and that of the exhaust-steam from T act at the same time.

Solvay in the same patent describes another apparatus for continuous distillation with a single column. This does not seem to be actually employed.

At the end of the distillation the exhausted liquid is run off by the cocks Z; and the bottom door I, which at the same time supports the bottom of the lime-cage P, is opened, so that the residue falls out of the latter. In order to separate the liquor, containing calcium and sodium chloride, from the suspended matter, Solvay

passes it through the self-acting decanting-apparatus, fig. 185. The hot liquor passes through the pipe C into a central pipe B, whence the steam escapes through the pipe D, while the liquor rises up in the vessel A and at the top runs over into the pipe F at E. The lime mud settles at the bottom, is scraped off the same

Fig. 185.



by scrapers moved by the hand-wheel H and taken out at I. The conical valve K, moved by the lever M and the rod N, prevents the fresh liquor from disturbing the settled lime mud. The distillation is best carried on in a partial vacuum; the gas, before reaching the pump, first passes through washing-apparatus for retaining any ammonia it may contain.

Solvay's still has been improved in some details by L. Mond (B. P. 715, 1883).

It is, of course, not the place here to treat of the manifold attempts for replacing the lime in the distillation of ammonia by magnesia, in order to be able to utilize the chlorine, otherwise lost

in the calcium-chloride liquor running to waste. All those attempts entirely belong to the domain of alkali and chlorine manufacture, and have no place in the manufacture of ammonium compounds for commerce, where lime is the agent exclusively used for the above purpose, and probably always will be.

Removal of Sulphides otherwise than by Lime, in the Manufacture of Liquor Ammoniæ.

Instead of employing lime for retaining the sulphides (in which case a large excess is necessary, as CaS is decomposed by prolonged boiling) some employ *ferric hydrate*, as in purifying gas. The reaction is:

$$Fe_2(OH)_6 + 3(NH_4)_2S = 2FeS + S + 6NH_3 + 6H_2O.$$

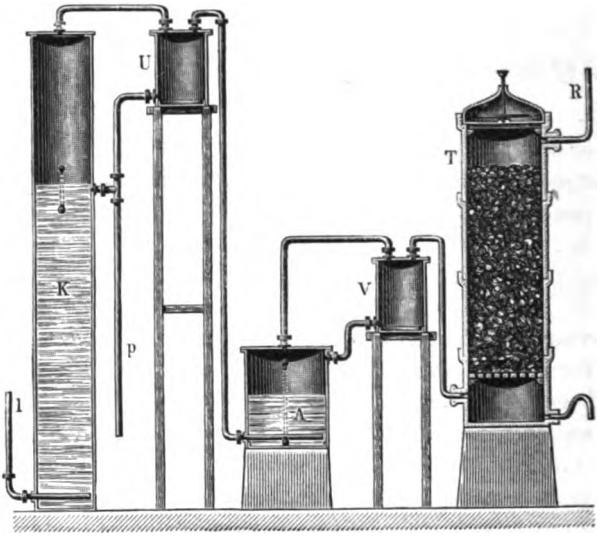
Thus ferrous sulphide, sulphur, and free ammonia are produced; the two former remain behind. The residue can be revivified till it is rich enough in sulphur to be utilized for vitriol-making, or for the sulphur to be recovered by distillation. For the latter purpose Gerlach (G. P. 229) employs superheated steam, as offering great advantages.

Sometimes *soluble salts of iron or manganese* are added to the gas-liquor before distillation, in order to remove the sulphide. The precipitate might be filter-pressed, and the residue revivified as just mentioned. But this process, like the former, is much less simple and cheap than the lime-treatment, especially in the form employed by Feldmann.

A special process for removing sulphuretted hydrogen from gas-liquor is that of Kunheim and Co. (G. P. 26422), which aims at fully utilizing the sulphur. The crude gas-liquor is treated in the cold state with a strong current of atmospheric air, divided into many jets. This dissociates the ammonium sulphide into ammonia and hydrogen sulphide, the latter being carried away by the air. The gaseous mixture is conducted through finely divided ferric hydroxide, and the hydrogen sulphide is here absorbed. For this purpose native hydrated oxide of iron, or an artificial precipitate, or even other hydrated metallic oxides may be employed. The ferric hydroxide is kept suspended in a dilute solution of alkaline earths. Fig. 186 illustrates the process. The gas-liquor is introduced by means of a force-pump through the pipe *p* into the

boiler K, into which a strong current of air is forced by means of a blast or injector through *l*. The gas-liquor mechanically carried away is retained in the safety-vessel U, and is continually returned

Fig. 186.



into K. The mixture of air, hydrogen sulphide, and a little ammonia is conducted by a perforated pipe into the vessel A, half filled with a mixture of ferric hydrate and lime-water. Here the H_2S is absorbed, but the FeS formed is at once changed by the air into free sulphur and regenerated ferric hydrate. The excess of air and some ammonia first pass through the safety-vessel V, where so much of the pasty mixture as has been mechanically carried away is retained and flows back into A. From here the gases pass through the stoneware coke-scrubber T, where the ammonia is absorbed by a shower of sulphuric acid. The air escapes through R into the atmosphere, or first into a chimney. The gas-liquor remaining in K, and now freed from sulphide, is in the usual way caustified by lime and distilled. The described process of absorbing hydrogen sulphide by a mixture of ferric hydroxide with lime, with a simultaneous introduction of air for re-converting the ferrous sulphide formed into free sulphur and ferric hydroxide, may also be employed for dealing with hydrogen sulphide from any other source. [It is only right to state that the absorption of sulphuretted hydrogen by a mixture of ferric or manganic hydroxide

and lime, suspended in water, was described by me as early as 1866, in the British patent No. 1108; and Weldon, in his patent of Aug. 18, 1871, and again in 1876, added to this the regeneration by air in the liquid state. The simultaneous passage of air, along with the H_2S, through the mixture of ferric hydroxide of lime was also tried by myself about that time, but nothing was published about it, as the experiments could not be followed out to a definite issue.]

Carriage of Liquor Ammoniæ.

This is generally effected in glass carboys, where the distance is not considerable or small quantities are concerned. The carboys must not be quite full, and must be kept in a cool place, lest they should be cracked by pressure of gas. They must be very tightly corked to prevent loss of ammonia by evaporation, which can be hardly altogether avoided when the liquor is kept in stock for some time. For large quantities wrought-iron drums are employed, which, however, give rise to red precipitates of iron oxides, and hence can only be employed for the crude article. The purer article can be sent out in tinned iron drums. Sometimes galvanized iron drums are used; but it would seem that the zinc coating must be gradually dissolved by the ammonia, especially if any air can enter.

Properties and Application of Liquor Ammoniæ (Caustic Ammonia).

The percentage of ammonia in this is nearly always ascertained by means of the hydrometer, for which the tables on pp. 582 *et seq.* may serve; but it must not be overlooked that these are valid only for the temperatures stated. In lieu of the figures for specific gravity, it is usual in Germany to employ the hydrometer of Baumé or Beck, in France that of Cartier; a table given in the Appendix will permit the reduction of these degrees to specific gravities.

Technically pure liquor ammoniæ ought to be colourless (even when exposed to the light for some time), clear, and not smelling too much of empyreuma. Sulphides ought to be entirely absent, as shown by lead-paper. Pure liquor ammoniæ for pharmaceutical purposes ought to be free from chlorides and cyanides (in which case, when it is neutralized by nitric acid, silver nitrate produces no opalescence), and should be almost free from empyreuma. The latter is especially perceptible on neutralizing the liquid.

Kupfferschläger * proposes proving the presence of tarry matters in liquor ammoniæ by the red colour which is produced by pouring a few drops of it into a test-tube containing a few cubic centimetres of colourless nitric acid diluted with a quarter of its volume of water. According to Wittstein †, the pink colour does not arise if the nitric acid be at once supersaturated with ammonia, but only on partial saturation, and it is destroyed by an excess of alkali. Both chemists ascribe it to the action of nitric acid on aniline &c. Lehmann ‡ many years ago made a similar observation.

H. Ost mentions § that *pyridine* can be detected by its smell when nearly neutralizing the ammonia. By distilling the liquid, collecting the distillate in hydrochloric acid, evaporating and extracting the residue with absolute alcohol, a solution is obtained containing but little ammonium chloride. This is removed by addition of platinum chloride, and on evaporation of the alcoholic filtrate the platinum-pyridine double chloride separates in characteristic forms.

Liquor ammoniæ is employed for numerous purposes—in pharmacy, for washing wool, dyeing, calico-printing, for the preparation of colouring-matters, especially "cochenille ammoniacale" and cudbear, and latterly for extracting indigo, for many chemicals, and especially for Carré's and Linde's ice-making machines.

Ammonium Chloride (Sal-ammoniac).

This salt formerly came from Egypt, and from the 13th century till late into the 18th century this was the only source of ammonium salts available in Europe (apart from the direct use of putrefied urine in dyeing &c.). In Egypt sal-ammoniac was made as a by-product in utilizing dried camels' dung for fuel.

The food of the camels to a great extent consists of plants containing a good deal of salt, and their urine contains some ammonium chloride ready formed. The principal portion is, however, only formed from the nitrogenous substances and the chlorides when burning the camels' dung, dried in the sun. The soot formed in burning was carefully collected and subjected to subli-

* Bull. Soc. Chim. xxiii. p. 256.
† Dingler's Journal, ccxiii. p. 512.
‡ Wagner's Jahresb. 1864, p. 195.
§ Zeitschr. f. analyt. Chem. xxiii. p. 59.

mation in special factories (one of which, in the delta of the Nile, was visited by the Jesuit Sicard in 1720). 40 lb. of soot are said to have yielded about 6 lb. of sal-ammoniac.

In other countries, where dried dung is also used as fuel, it has been sometimes attempted to manufacture sal-ammoniac by mixing salt with the dung before burning it, and collecting the soot. This manufacture does not, however, seem ever to have had any considerable extension, except in India, whence a good deal of sal-ammoniac was formerly exported *.

In Europe sal-ammoniac is said to have been first obtained by the destructive distillation of oil-cake (a remarkably wasteful manufacture!) and from the soot formed in the burning of coal.

The first sal-ammoniac factory in Germany was that of the brothers Gravenhorst at Brunswick, founded in 1759. In Scotland it seems to have been manufactured since about 1750.

The present manufacture of ammonium chloride is carried on in various ways—either by direct saturation of gas-liquor or similar ammoniacal liquids (*e. g.* from the manufacture of bone-charcoal, or from putrefying urine), or by decomposing ammonium sulphate with sodium chloride, or by passing ammonia vapour into hydrochloric acid.

This last process is not much used. It has the drawback that no metal vessels, not even lead ones, resist the action of hot hydrochloric acid; and much acid and ammonium chloride is carried away by the hot vapours. Still this process is carried on at some places in France. More rational is the plan followed at a French works (by the Compagnie Lesage), where the concentrated solution of ammonium carbonate and sulphate, obtained by one of the above-described apparatus (*e. g.* Mallet's or Grüneberg's), is mixed with hydrochloric acid in a vessel lined with lead and provided with a pipe for carrying away the vapours, in such manner that both liquids run in at the same time and that a nearly neutral but faintly acid liquid is formed. Towards the end of the operation the temperature rises considerably, and there is much more danger of ammonia being carried away by the vapours, which must of course be dealt with in the ordinary manner to destroy the hydrogen sulphide. Whenever the vessel

* A detailed account of the manufacturing processes formerly used in Egypt and India for making sal-ammoniac is contained in 'Chemistry as applied to the Arts and Manufactures,' London (Mackenzie), vol. i. p. 188.

is full the supply is stopped, and the liquor is concentrated by a steam-coil up to the crystallizing point. The crystallization takes place in vessels lined with lead, and the crystals turn out quite white, if made from sewage. As very large crystals are not liked in trade, the contents of the crystallizers are stirred up two or three times a day. Naturally the size of the crystals also depends to a great extent on the concentration of the solution. When a solution of ammonium chloride is boiled down in iron vessels, as is sometimes done (especially in England) in order to allow of direct firing and to economzie fuel, the liquid must always be kept alkaline, and the loss of ammonia occurring during the evaporation by the dissociation of a little ammonium chloride must always be made up. If the liquid once becomes acid it quickly dissolves iron in the form of ferro-ammonium chloride, which is not decomposed by an excess of ammonia. Evaporating in lead is dearer, but much safer if contamination with iron is to be avoided. Even metal cocks must be dispensed with, and must be replaced by india-rubber tubing and pinch-cocks.

At some English works sal-ammoniac is still made by direct saturation of gas-liquor with hydrochloric acid, mechanically agitated. The escaping noxious gases are conveyed into the boiler-fire and burned. The faintly acid solution is left to settle; in three or four days the tar has separated out at the bottom of the vessel. Sometimes it is necessary to pass the liquid through canvas filters. The solution of ammonium chloride, still dark brown, is evaporated by direct fire in iron pans, and is always kept neutral or faintly alkaline by means of a little lime, chalk, or ammoniacal liquor. During the evaporation tarry oils are again separated, and are skimmed off along with a little ferric oxide. The vapours ought to be condensed, as they cause a considerable nuisance. When the liquor has attained the required strength, it is run into tubs 8 feet wide and 2½ feet deep, where its crystallization is finished in 8 or 10 days. Every 6 or 8 hours it is stirred up in order to get small crystals, which are better for subliming. Finally the mother-liquor is run off by a plug-hole in the bottom, which is best made to slope to one side.

In order to make ammonium chloride from *sulphate*, a concentrated solution of the latter is mixed with an equivalent quantity of common salt and the whole is well agitated and boiled down,

during which process monohydrated sodium sulphate is precipitated and ammonium chloride remains in solution:

$$(NH_4)_2SO_4 + 2\,NaCl = Na_2SO_4 + 2\,NH_4Cl.$$

The sodium sulphate is fished out with perforated spades and drained on copper plates, the liquor always running back into the pan. The salt is washed with a little water. The evaporation is continued till no more coarse crystals fall down and the liquid begins to be covered with an opalescent pellicle of salt, which shows that the sodium sulphate is nearly all removed. The liquid is now allowed to cool in leaden vessels; and the crystallizing ammonium chloride is first washed with a solution of the pure salt, then with pure water.

Th. Schmidtborn (Amer. Pat. 330155) decomposes ammonium sulphate and *potassium chloride* into potassium sulphate and ammonium chloride. He describes his process as follows *:—In a lead-lined tub, with false bottom and agitating-gear, 2½ tons ammonium sulphate are dissolved in water or in the washings of potassium sulphate up to sp. gr.=71° Twaddell. The liquor is heated to boiling, and the exactly equivalent quantity of potassium chloride is put in, with constant agitation. The boiling is continued for another 10 minutes; the liquor is allowed to settle for half an hour and is then run off. The potassium sulphate for the most part remains behind on the false bottom, and can be freed from ammonium salts down to ½ per cent. by washing. Thus 70 per cent. of the total potassium sulphate are recovered. The washings are used for making a fresh solution of ammonium sulphate. The hot liquor on cooling deposits more potassium sulphate, and a further quantity on concentration. By a second concentration and cooling down, a mixture of salts is obtained in two distinct layers; the upper three-fifths consisting of 94 per cent. ammonium chloride with 6 per cent. potassium and sodium sulphate and sodium chloride; the lower two-fifths consisting of 78 per cent. ammonium chloride and 22 per cent. potassium sulphate. The upper layer can be converted into 98 or 99 per cent. ammonium chloride by mere washing; the lower by recrystallizing. For the latter object the salt is suspended in perforated trays in boiling liquor, which dissolves out the ammonium chloride within a few minutes; the crystalline potassium sulphate remains behind on

* Chem. Zeit. 1886, p. 1499.

the trays and is lifted out in them. On cooling, the ammonium chloride crystallizes out and is drained by means of a centrifugal machine, as well as the potassium sulphate. The former is also stove-dried; the latter is sold as it is. This process, which has been carried out by the inventor, is claimed by him as an improvement upon the analogous process with sodium chloride, because there is no partial re-decomposition on the liquors cooling down. He also claims that the value of the potassium chloride is more than covered by that of the sulphate obtained; but this surely holds much more in the case of the sodium salts.

Kuentz has proposed to make sal-ammoniac by direct distillation of ammoniacal liquor into an acid solution of phosphate of lime, produced by dissolving native phosphate of lime in hydrochloric acid:

$$Ca_3(PO_4)_2 + 4\,HCl = CaH_4(PO_4)_2 + 2\,CaCl_2.$$

The reaction taking place with the ammonium carbonate distilled into the solution, or added in the shape of concentrated liquor, produces a precipitate of dicalcium phosphate and calcium carbonate, which is a much more valuable manure than the native phosphate, and a solution of ammonium chloride. The object of this process is to save the acid required for making superphosphate or "precipitated phosphate," as this acid is altogether turned into sal-ammoniac; but the process does not seem to have found a practical application. Its theoretical equation would be:—

$$CaH_4(PO_4)_2 + 2\,CaCl_2 + 2(NH_4)_2CO_3 = \\ = 2CaH\,PO_4 + CaCO_3 + 4\,NH_4Cl + CO_2 + H_2O.$$

Another process proposed by Kuentz consists in treating the raw gas-liquor with impure ferrous chloride, made from pyritous schist and common salt. There is thus obtained a solution of ammonium chloride and a precipitate of ferrous carbonate and oxide mixed with a little sulphide, which is an excellent material for purifying coal-gas. In this process no noxious gases are given off.

Another process is one in which "concentrated gas-liquor" (p. 621) is mixed with a solution of calcium chloride (which is a waste-product of many chemical operations and without any value) till all the lime is precipitated; the mass, passed through a filter-press, yields cakes of calcium carbonate and a solution of ammo-

nium chloride, which should be acidified with hydrochloric acid, to destroy any sulphide. The calcium carbonate carries down most of the impurities; so that even ammoniacal liquors from the destructive distillation of bones and other animal matters can be treated in this way for pure ammonium chloride.

Gentles (B. P. 2224, 1878) distils the ammonium carbonate &c. from gas-liquor into a crude solution of calcium chloride, contained in a vessel with agitating-gear. The solution is separated from the precipitate, is acidified in order to precipitate any arsenic as trisulphide, and the clear filtrate is again made alkaline with ammonia, to precipitate any iron as oxide. These processes, founded on the application of calcium chloride, would seem to deserve attention.

A very peculiar process is that of Th. Heskin (B. P. 2491, 1884). He decomposes sodium borate by sulphuretted hydrogen, dissolves the separated boric acid in strong liquor ammoniæ, and decomposes the ammonium borate with common salt, whereby sodium borate is regenerated.

The *crude ammonium chloride* is coloured more or less dark by tarry matters, and contains other impurities, especially ammonium sulphate and thiosulphate, as well as moisture. It is dried in layers 4 inches thick, on metal plates heated by the waste heat of the subliming-pans, but not to the point of volatilization. Here the water and free acid are volatilized, and the tarry matters are mostly carbonized. The roasted salt is of a grey-white colour, and ought to be conveyed as quickly as possible into the subliming-pots, lest it should again attract moisture. If the crude salt has been made by direct saturation of gas-liquor with hydrochloric acid (a process which ought to be given up as quite irrational, and as causing a great nuisance), in drying or roasting it produces a very bad smell, which is absent when the salt has been made from distilled ammonia.

Sometimes the *subliming* is done in long rows of earthenware pots or glass carboys. This is the process used in Egypt and other oriental countries, and it is still exclusively practised in France, since the buyers there demand the small cakes obtained by this process. But this is expensive, on account of the labour and the loss of the vessels in each operation. Hence in England iron pots are exclusively used, either cast in one piece or composed of several pieces, of 3 to 9 feet diameter. Large pots are far preferable

to small ones, as the latter require hardly less fuel, labour, and time for working off than the former. They are lined with firebricks, and are heated by a fire from below and by annular flues all round. Their bottom is, by preference, concave, so as to present a larger heating-surface. The pots are covered with concave plates, furnished in three places with rings for chains, by means of which they can be lifted off by a travelling crane &c. The covers are perforated in the centre; the aperture is closed by an iron rod, which is removed from time to time to allow the permanent gases to escape. They are covered with some non-conductor of heat. Pots 3 feet wide hold 10 cwt., those 5 feet wide 15 to 18 cwt., and those 9 feet wide 2 to 2½ tons of salt.

The operation must be exactly regulated. At first a sharp fire is made; but this is slackened directly the sublimation commences, since at a very high temperature too much empyreumatic matter is evolved and disturbs the solidification of the salt. At too low a temperature the sublimate is loose and not transparent, which makes it difficult to sell. The cover ought to be at such a heat that a drop of water begins to boil on it and evaporates quickly. The first layer adhering to the cover is always brownish, probably because a little water always remains in the roasted salt, which condenses on the cover and loosens ferric oxide. Later on a coloration may be caused by ferric chloride. The sublimation may last from 5 to 9 days, but is usually interrupted every week by lifting the cover, the fire having been damped up some time before. The sublimation is not driven to the last; for then the temperature would rise too high, the carbonaceous impurities would be decomposed, and the vapours would injure the appearance of the sal-ammoniac. On the cover is found a layer from 2½ to 4 inches thick, which is knocked off. The above-mentioned brown stratum is hacked off with a hatchet or planed off.

The French subliming-process is illustrated by figs. 187 and 188. It is carried on in earthenware pots P, about 18 inches high and 12 to 14 inches wide, of which about 20 are placed, in two rows, in a galley-furnace heated at one end. The pots stand on an arch, perforated by pigeon-holes, *o o*; they are supported at two-thirds of their height by the cast-iron plate F, on which a layer of sand is spread right up to the top of the pots. After being charged with dry crystallized ammonium chloride, which is sometimes mixed with about 20 or 30 per cent. of animal charcoal, they are

placed in the furnace, covered up with sand, and at first gently heated to avoid cracking. The moisture still present escapes through the openings, *s s*, and soon the thick white vapours of sal-ammoniac

Fig. 187.

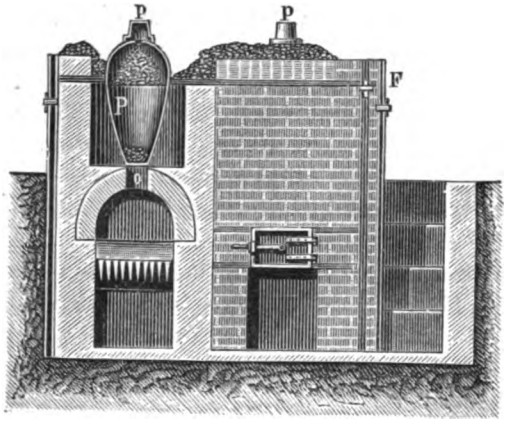
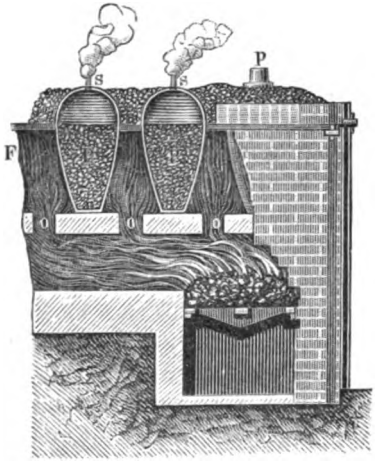


Fig. 188.



appear, whereupon an ordinary flower-pot, *p*, is put on as a cover. The sublimate collects partly in the upper portion of the pots P, partly in the flower-pots, *p*. The openings, *s s*, gradually get stopped up; and towards the end of the operation, when the fire has to be increased so as to produce the dense and translucent

appearance of the product required in commerce, there is a certain pressure in the apparatus. In order to obtain sufficiently large cakes, the pots must be charged several times over again. For this purpose the openings are cleared again, and the operation is repeated. After two or three charges the cakes are large enough; the pots are now taken out when sufficiently cool, and are broken in order to get out the sublimate. The whole takes about two days. In some places, in lieu of earthenware pots, glass flasks or carboys are used on account of cheapness. These are usually about a foot wide and two feet high, and contain 20 lb. of the mixture of dry ammonium chloride and charcoal. They are placed in a double row of 8 or 10 each in metal pots, heated by a galley-furnace. The pots serve as sand-baths, and the flasks are about two thirds within the pot; the last third projects outside, but is covered with a layer of sand up to the neck, which is covered with a piece of sheet-lead. When this appears covered with a glassy sublimate of sal-ammoniac, the projecting part of the flask is cleared of sand, and care is taken lest the lead should adhere too fast to the flask, by knocking on its lower side from time to time. When the sublimate is glass-like, and the lead plate, on knocking from below, is no longer lifted up by the vapours evolved, it is left quietly on the top; but the upper opening must never be allowed to become entirely stopped up, which is prevented by boring in with a pointed iron. The operation lasts from 12 to 16 hours. The lead covers are then taken away, and are replaced by corks or by tufts of cotton-wool, and the whole is allowed to cool down slowly. During the cooling the sal-ammoniac expands and cracks the glass. The cake, freed from glass, is scraped off with a knife, to remove all dirty places, and is packed in the shape of loaves; it is crystalline and perfectly white.

The French sal-ammoniac being thus made in earthenware or glass vessels, is purer than the English article sublimed in iron pots. The destruction of the subliming-vessels at each operation makes it a costly product; but it might no doubt be made much more cheaply in stoneware vessels consisting of two parts, which would stand a number of operations.

Some consumers, especially in France, require the sublimed sal-ammoniac to look as grey and dirty as that formerly made in Egypt from camels' dung; this is effected by adding some greasy matter to the salt before sublimation, or in small portions during

the operation, so that some soot gets mixed with the sal-ammoniac. Otherwise it ought to be white, transparent, of fibrous texture, and firm, not porous and light. Sometimes a few per cent. of monocalcium phosphate or of ammonium phosphate are mixed with the salt before subliming, to retain any iron.

Calvert proposed, in order to make the sublimation cheaper and continuous, and to obtain the product in a shape more convenient for use, to dry the muriate of ammonia very briskly and distil it from a set of fireclay retorts, alternately charged, into large brick chambers covered with a smooth coating of cement inside, on which the sal-ammoniac would be deposited as a fine powder. This process, which looks very rational indeed, was tried on the large scale, but was given up and is not in use anywhere at present, probably because the consumers insist upon the fibrous transparent texture of the product, which they believe (although erroneously) to guarantee its purity. Calvert also tried adding animal charcoal and phosphates before subliming; but his sal-ammoniac was never free from iron.

Commercial sal-ammoniac appears in the form of cakes or disks, weighing from 10 to 40 lb., sometimes up to one cwt., white, translucent, of fat-like brilliancy, hard and sounding. They are formed of parallel layers of a fibrous texture.

Besides sublimed sal-ammoniac, the crystallized salt, usually called *muriate of ammonia*, is also found in the trade, at a much lower price. To obtain this, the crude salt is once or more times recrystallized, and the solution each time filtered through animal charcoal. It is also made into the shape of loaves, the crystals being stirred up to a paste with a hot saturated solution, and the whole being allowed to solidify in conical sugar-moulds of glazed earthenware. The opening at the bottom is at first closed up by a plug, which is removed after a few days; the mother-liquor then drains off. The loaves are taken out by inverting the moulds, and are dried in a stove; they turn nearly as hard as loaf-sugar. Most ammonium chloride, however, is sold in the form of sublimed sal-ammoniac. The consumers insist upon having it in this shape, although it generally costs twice as much as the crystallized salt, and is no better. An attempt made by the French Company Lesage to replace it by strongly compressed cakes of crystallized salts, in disks of 4 inches diameter and 1 inch thick, failed for want of support from the buyers.

Ammonium chloride is chiefly used in pharmacy, in soldering, in galvanizing iron, for making the ordinary rust-cement (from 100 parts iron filings, 2 brimstone, and 1 sal-ammoniac), in dyeing and calico-printing, and in the manufacture of colours. For the latter purpose it should in general be free from iron. Formerly it was believed that this was always the case with colourless sal-ammoniac; but Wurtz has shown that only ferric chloride is indicated in sal-ammoniac by the ordinary reagents, while ferrous chloride cannot be discovered either by the colour or by the ordinary reagents. The ferrous can be formed from the ferric chloride by the reducing action of sal-ammoniac itself, thus:—

$$3\,Fe_2Cl_6 + 2\,NH_4Cl = 6\,FeCl_2 + 8\,HCl + 2\,N.$$

In order to make a product entirely free from iron, a little chlorine gas is passed through the boiling-hot solution of ammonium chloride (an excess of chlorine would produce that fearfully explosive substance, nitrogen chloride); ammonia is added, which precipitates all the iron now present as peroxide; the liquid is quickly filtered and crystallized. A salt free from iron is said to be obtained also by adding a little calcium phosphate before sublimation (see preceding page).

A not inconsiderable quantity of crystallized ammonium chloride is used for feeding the Leclanché cells very generally employed in telegraph-offices &c. For this purpose it should be free from lead, which is very injurious for the working of the cells, and should therefore be freed from metals by ammonium sulphide.

Ammonium Carbonate.

Commercial carbonate of ammonia (sal volatile), as has been explained on p. 587, is really a mixture or a compound of ammonium bicarbonate and carbamate, and as such is always formed on subliming. Hence the name frequently used for it, "ammonium sesquicarbonate," is incorrect, although the salt actually often contains four molecules of NH_3 to three of CO_2.

In 1870 Divers found the article then manufactured to contain more ammonia, in the proportion of three molecules of NH_3 to two of CO_2; but in 1886 Hanekop and Reissmann, on the contrary, found an article consisting of one molecule of NH_3 to one of CO_2 (p. 586), that is, really, ammonium bicarbonate; and Topf, in

1887, has confirmed this with several samples of the commercial article analyzed by him (Zeitschr. f. analyt. Chem. xxvi. p. 158). Evidently different mixtures or compounds of ammonium salts have come into the trade, at different times, and probably even at the same time, under the name of "ammonium carbonate."

Ammonium carbonate is formed in the destructive distillation of animal matters, and is often found as a solid deposit in the refrigerator, if the substances employed have been dry. This deposit, which forms brown crusts, was formerly known as "salts of hartshorn," and was always accompanied by a watery liquid, a saturated solution of ammonium carbonate, known as "spirits of hartshorn." Both are very much contaminated with tarry products, and cannot be purified by one redistillation, but only by a third distillation with bone-black. This manufacture is rarely carried out now.

Commercial ammonium carbonate is now usually made by mixing ammonium sulphate with calcium carbonate and subliming. Calcium sulphate remains behind in the retort; and the mixture of ammonia, carbon dioxide, and aqueous vapour (which must not be absent) condenses on cooling to solid carbonate of ammonia. A mixture of 1 part ammonium sulphate with $1\frac{1}{2}$ or 2 parts of finely ground chalk, sometimes with a little charcoal powder, is heated in horizontal cylindrical cast-iron retorts, several of which are usually heated by the same fire, like gas-retorts. At first the heat should not be great; but at last it must attain redness.

The vapours are conveyed by a wide pipe into lead chambers, usually two or more in succession, provided with a door for the removal of the salt. From the last chamber the vapours pass through sulphuric acid, preferably trickling down in a small leaden coke-tower. In the chambers the condensation is effected solely by air-cooling; but they may be surrounded by a jacket to cool them by water. Several operations are performed in succession, till a sufficiently thick crust has formed, which is loosened by blows outside with a hammer, and is completely broken off after opening the doors. This crust must not be allowed to become too thick, as otherwise the air-cooling will be too imperfect and the salt will become too hard and difficult to detach.

A convenient plan is to employ five retorts, 18 inches in diameter and 7 feet long, heated by one fire, with two condensing-chambers, each 8 or 10 feet long and wide and 7 feet high. The retorts may

be charged alternately every eight hours. Each retort-cover has an aperture for a rake, to stir up the mass during the operation. The process in such an apparatus can go on for a fortnight before the chambers need be emptied, when the men adopt the precaution of tying sponges drenched in vinegar in front of their mouths and noses. During the work care must be taken lest the connecting pipes between the retorts and chambers get choked up.

In the bottom of the condensing-chambers is a pipe for running off a little solution of ammonium carbonate, formed from the excess of moisture; here also a little steam escapes.

The product of this first operation is still very impure, at least if crude ammonium sulphate has been employed; it is then discoloured by tarry matters, and is sometimes sold as "ammonium carbonicum pyro-oleosum." It also mostly contains a little chalk or calcium sulphate carried over. According to Divers (p. 587), whose observations have been confirmed by myself, this product has not the composition of commercial ammonium carbonate, no ammonia escaping during the distillation, but is normal ammonium carbonate, $(NH_4)_2CO_3$, or probably, rather, ammonium carbamate, $(NH_4)CO_2(NH_2)$. With a leaky and warm receiver, however, acid carbonate is formed, and the latter, that is the commercial salt, is always produced in resubliming the first product.

This product, being too impure, is generally converted by resubliming into a white salt, forming fibrous transparent cakes 2 inches thick. This can be done, with hardly any expense, by the waste heat of the retort-furnace, which travels underneath a row of iron pots covered with lead cylindrical caps. The crude salt is put into the pots, along with a little water (without which the pure salt would not be transparent). Sometimes the pans are not exposed to the direct fire, but are placed in a common water-bath, heated by the waste heat of the retort-fire. A temperature of 70° suffices for resubliming; and it is best not to exceed this, because the salt turns out finer and less is lost by volatilization. The lead caps into which the salt is to sublime are made by rolling a sheet of lead into the shape of a cylinder, about 12 inches wide and 2 feet 6 inches high, covering this at the top with a piece of sheet-lead and pasting up the joints with paper. When the sublimation is finished, the lead is unrolled and the cake of salt can be taken out at once.

Another apparatus for resubliming * consists of an iron pan 2 feet 6 inches wide at the bottom and 2 feet at the top, 15 feet long, and 2 feet 6 inches high, in the cover of which there are eight 12-inch holes, on which are placed conical lead caps, 2 feet 6 inches high, kept in their shape by clamps or wedges. With these it is possible to work 14 days uninterruptedly. Then the clamps or wedges are loosened, and the mass is taken out; but it must be scraped off clean where it adheres to the lead. The salt is mostly packed in stone jars. In the iron pan remains some liquid, most of which is left behind for the next operation.

The different qualities of white ammonium carbonate found in commerce seem to be obtained by heating more or less quickly, and by putting more or less water into the charges.

The usual process for making ammonium carbonate, as just described, does not appear to be quite rational. In the finished salt there is $1\frac{1}{2}$ times (or, in the salt analyzed by Divers, $1\frac{1}{3}$ times) as much carbon dioxide as in the neutral salt; but according to the conditions of the process there is only enough CO_2 for the latter. Hence a large quantity of ammonia must go away in the uncombined state. This might be remedied by passing carbon dioxide into the subliming-apparatus; even an excess of this would not interfere with the formation of the ordinary ammonium carbonate.

(This suggestion, which was thrown out in the 1882 edition of this work, has since been acted upon successfully by at least one manufacturer of carbonate of ammonia.)

Other Methods for Manufacturing Ammonium Carbonate.

Kunheim & Co., of Berlin, manufacture this salt in the most direct manner, by bringing together the gaseous mixture from the distillation of gas-liquor with carbon dioxide in lead chambers, and thus producing the commercial salt.

Seidler (G. P. 26633) distils crude gas-liquor over limestone or dolomite, whereby the fixed ammonium salts are decomposed, so that the distillate contains, besides ammonium carbonate, only a little sulphide. This is removed by treating the concentrated

* Bell, Chem. News, xii. p. 303.

aqueous solution with CO_2, and the commercial salt is produced from the precipitated crude ammonium carbonate by sublimation*.

F. C. Glaser (B. P. 5761, 1884) heats salts of ammonia with equivalent quantities of sodium carbonate, to which a small quantity of bicarbonate has been added. The reaction is said to take place in a more perfect manner. [This will be too costly!]

F. C. Teed (Journ. Soc. Chem. Ind. 1885, p. 709), from experiments on a small scale, makes a proposal similar to Seidler's, viz. running a solution of ammonium chloride slowly down a tower filled with small pieces of calcium carbonate, steam being blown up at the same time. Solid ammonium carbonate forms at the top.

Wächtler (G. P. 34393) injects a spray of ammoniacal liquor, by means of a compressor, into a red-hot retort filled with calcium carbonate.

A method formerly employed by Kunheim & Co. consisted in subliming ammonium chloride with barium carbonate, to obtain barium chloride as a by-product.

Pure ammonium carbonate (compare its properties, p. 587) is quite white, and at a fresh fracture shining and transparent, but is soon covered in the air with a fine dust of ammonium bicarbonate, ammonia being given off. On being heated it should volatilize completely and without empyreumatic smell; tarry matters are betrayed by a brown colour of the aqueous solution. The salt intended for analytical chemists should, after being neutralized with nitric acid, give no reaction with silver nitrate for chloride, or with barium salt for sulphate. Lime is indicated by a fixed residue and by precipitation with ammonium oxalate; lead (which is to be avoided when the salt is to be employed as a baking-powder) by means of hydrogen sulphide. Sometimes thiosulphate is found by dissolving in acetic acid and adding silver nitrate, which produces a white precipitate, turning brown in a few moments.

This salt is principally employed for scouring wool, as a general detergent, in dyeing, as smelling-salts, as a baking-powder, in medicine, &c. The importation into Germany in 1885 was 613 tons, the exportation 927 tons.

* Details of the apparatus are given in Dingler's Journal, cclii. p. 476, and in the Journ. Soc. Chem. Ind. 1885, p. 112.

Ammonium Phosphate.

Both the acid phosphate or monammonium phosphate, ($NH_4H_2PO_4$), and the intermediate phosphate, or diammonium phosphate, $(NH_4)_2HPO_4$, have recently become commercial products.

According to Lagrange *, these salts are made from superphosphate, manufactured in the usual way by treating mineral phosphates with sulphuric acid. This product is lixiviated with water and with the aid of steam injected into the mixture, in a methodical way, whereby liquors of 25° Baumé (=42° Twaddell) are obtained. The residue, consisting principally of calcium sulphate, is thrown away. The solution contains free phosphoric acid, monocalcium phosphate, calcium sulphate, and a little free sulphuric acid. First the latter is removed by adding a slight excess of barium carbonate; the precipitated barium sulphate is separated by filtration, and can be utilized as a paint. The filtrate, which now only contains phosphoric acid, monocalcium phosphate, and very little monobarium phosphate, is neutralized by ammonia in slight excess. This precipitates all the lime as basic phosphate, which is washed and used over again, along with the native phosphate, for manufacturing superphosphate. The filtered solution contains monammonium (acid) phosphate, and will test about 20° Baumé (=32° Tw.). It should be at that concentration to effect the precipitation of the biammonium phosphate, in the following manner:—The above liquor and liquor ammoniæ (of 22° Baumé=0·921) are gradually mixed in small vessels, in the proportion of $1\frac{1}{2}$ equivalents of NH_3 to 1 equivalent of monammonium phosphate. The biammonium phosphate at once separates out as a crystalline mass; but the vessels must be closed, to prevent the escape of ammonia, which is all the more likely to take place, as the reaction produces a rise of temperature. After cooling, the contents of the vessels form a thick paste, which is submitted to hydraulic pressing. The mother-liquor is used for the manufacture of ammonia; the cakes consist of pure $(NH_4)_2HPO_4$, and are sold to those sugar-refiners who employ the purifying-process of Lagrange.

Ammonium Sulphocyanide (Thiocyanate).

This salt has lately come into somewhat extensive use, especially in dyeing and calico-printing, both directly and as a starting-

* Vincent, 'Industrie des produits ammoniacaux,' p. 104.

point for the preparation of other sulphocyanides*; hence it is manufactured on an industrial scale. We pass over its preparation by synthetical method †, and only mention its recovery from ammoniacal gas-liquor. It remains behind when the volatile ammonium compounds are expelled by steam. From this residue cuprous sulphocyanide can be obtained by adding a mixed solution of the sulphates of iron and copper. This was done by P. Spence ‡, who, after washing the precipitate, decomposed it by ammonium sulphide into copper sulphide and ammonium sulphocyanide. Similar to this, but hardly preferable, is the process of Storck and Strobel §, who saturate gas-liquor with hydrochloric acid and precipitate the sulphocyanide by a mixture of cupric chloride and sodium bisulphite. The precipitate of cuprous sulphocyanide is washed, boiled with a solution of barium hydrate, and the barium sulphocyanide allowed to crystallize. Phipson || mentions another process known in London, but does not say in what it consists. The thiocyanate is especially easy to recover when applying the Claus process for purifying gas; it is found as a sodium salt in the residual liquor from distilling off the ammonia by means of caustic soda, and is recovered by evaporation, or as precipitation, in the state of cuprous thiocyanate. The amount of sodium thiocyanate is 2·3 lb. per ton of coal.

We have seen before (p. 550) that ammonium sulphocyanide occurs in large quantities in the ammonium salts made by lixiviating *spent oxide* from the purifiers. It should be possible to separate the sulphate from the sulphocyanide by fractional crystallization. As a rule, 10 to 30 per cent. of the latter salt is present in the total ammonium salts (comp. Gasch, Chemiker Zeitung, 1886, p. 214).

According to a patent of Marasse (G. P. 28137) the spent oxide, which after lixiviation still contains a great deal of sulphocyanide,

* Compare Storck and Strobel, Dingler's Journal, ccxxxv. p. 156; Glenck, ibid. ccxli. p. 599.

† Compare especially Tscherniak and Günzburg's German patent, No. 3199; Dingler's Journal, ccxxxii. p. 80. A new patent was taken out by them in 1881; and an exact description of their newest plant is found in the 'Bulletin de la Société industrielle de Mulhouse,' 1882, p. 77. Their factory has since ceased working.

‡ Chem. News, xviii. p. 119.

§ Dingler's Journal, ccxxxv. p. 156.

|| Chem. News, xviii. p. 131.

is heated in a closed vessel, with an excess of lime and water, to a temperature exceeding 100° C. The products of this treatment are ferrous sulphate and calcium sulphocyanide, the latter of which is recovered by lixiviation, and serves for preparing other sulphocyanides.

Estimation of Ammonia, free or combined.

We have already (p. 571 *et seq.*) treated of the valuation of gas-liquor; but we have yet to describe that of the sulphate and the other ammonium salts, and the preparation of the standard liquids.

The processes formerly in use for estimating ammonia, especially as ammonio-platinic chloride, are very seldom used now. For pure liquor ammoniæ the hydrometer is sufficient; but it is not so when foreign salts are present, which make the percentage of ammonia appear too low. The only certain process is:—estimating the ammonia directly; best of all, volumetrically. We have already seen (p. 572) that this can be done directly not merely with free ammonia, but also with ammonia combined with weak acids (CO_2, H_2S). If combined with strong acids, it must first be set free by treatment with a fixed alkali; and consequently this is the only suitable method for estimating the ammonium sulphate. For this purpose the apparatus shown in fig. 145 (p. 574) can be strongly recommended.

The following details of the process have been found most suitable at the large works of Kunheim & Co., near Berlin. The bulk-sample is well ground up, the whole of it passed through a sieve with about 8 meshes per linear inch, and a small sample taken from it. Of this about 15 grams are weighed, dissolved to 500 cubic centimetres, 50 c. c. of this introduced without filtering into a 300-c.c. flask, and distilled with about 15 c. c. caustic-soda solution of sp. gr. 1·25 for three hours; the evolved gas is absorbed in 50 c. c. of seminormal standard acid, and titrated back with seminormal soda solution till purple.

As standard acid oxalic acid has been frequently recommended, but not justly. It is difficult to obtain it perfectly pure, and impossible to make sure that it contains neither too much nor too little water; hence the acid must always be tested in other ways. It is therefore best to employ at once, as cheaper and more stable, sulphuric or hydrochloric acid. The latter is preferable, since its

strength can be exactly estimated in two different ways, viz. by titrating a known weight of freshly ignited pure sodium carbonate, and gravimetrically by means of silver nitrate. The standard acid is either made normal, so that 1 c. c. contains 0·049 gram SO_4H_2 or 0·0365 HCl, and indicates 0·017 gram NH_3, or else it is made $\frac{1}{2}$, $\frac{1}{5}$, or $\frac{1}{10}$ of that strength. The standard acid is kept in large bottles protected from great changes of temperature; whenever smaller stock-bottles or the burettes are to be filled with it, the large bottle ought to be agitated in order to mix its contents with any moisture evaporated and again condensed in the empty upper part of the vessel. The burettes employed are always Mohr's (fig. 189), preferably with Erdmann's float (fig. 190). As standard alkali for retitrating the acid partly saturated by the evolved ammonia, some chemists prefer ammonia or caustic baryta, not caustic potash or soda. Normal ammonia would lose too much NH_3 on keeping; but seminormal ammonia (=0·0085 gram NH_3 per c. c.) keeps in well-stoppered bottles a very long time without change, and still more so quinti- or decinormal liquid. From time to time its strength should be controlled by standard acid. The advantage of ammonia is that it does not attract carbon dioxide, like caustic potash or soda, which makes the passage from one colour into the other much more distinct. When employing methylorange as an indicator, this advantage disappears, since this indicator is not affected by CO_2.

In agricultural laboratories especially, baryta-water is very much employed, which in the nature of things must be free from carbonic acid, and hence gives very sharp final reactions. It cannot very well be made more than quintinormal; and care must be taken that it is not changed by attracting CO_2 from the air, which would precipitate baryta as carbonate. This is done by means of an apparatus* in which the burette is filled by opening a lateral pinch-cock; the air required to replace the baryta-water running out of the stock-bottle is deprived of CO_2 by soda-lime.

If litmus is used with baryta-water, the end is attained when the red has changed into purple for the *first* time and remains so when the liquid is shaken. After a little time the red reappears again, which should not be taken into account.

* Shown in Lunge's 'Sulphuric Acid and Alkali,' vol. i. p. 46.

Far preferable to litmus as an indicator is "methyl-orange" (comp. p. 572). In this case oxalic acid is excluded as standard

Fig. 189.

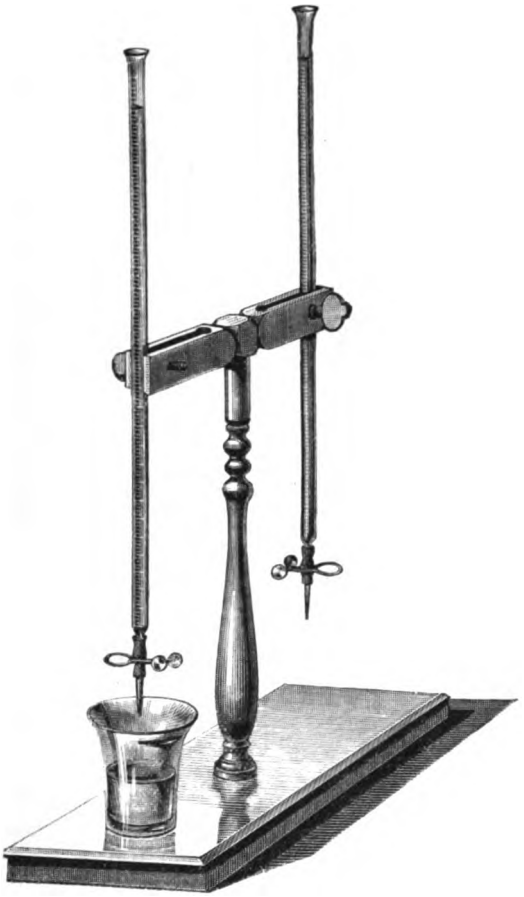


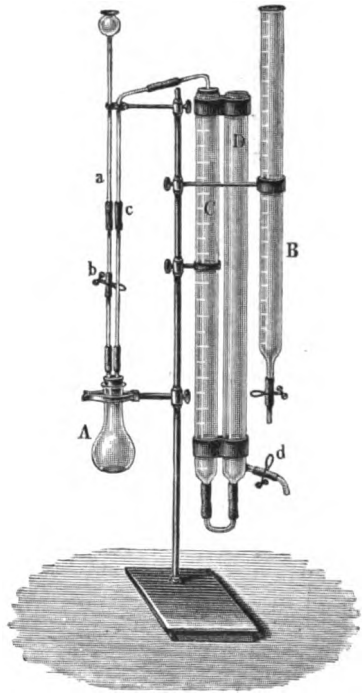
Fig. 190.

acid; but for retitrating a solution of soda or potash can be employed without any special precautions against attracting carbonic acid, since this does not interfere with the delicacy of the test; and thus titration with caustic potash or soda, with methyl-orange as indicator, is the most convenient of the methods described.

Some agricultural chemists estimate the ammonia by combustion

with soda-lime, in the way usual in organic analysis; but this is not at all to be recommended. Where many estimations have to be made, some prefer Knop's azotometer (fig. 191), which is founded on the fact that a solution of sodium hypochlorite containing

Fig. 191.



bromine, or of sodium hypobromite, in the presence of a large excess of alkali, almost instantaneously liberates all the nitrogen of ammonia salts. Such a solution is made by dissolving 100 grams of caustic soda in 250 cub. centim. of water, cooling the liquid (best by ice), and running in, with constant stirring, 25 grams of bromine. This solution does not keep very long, but decomposes, oxygen being given off. The nitrogen is liberated in the flask A, containing, up to a mark in its neck, 100 c. c.; it is measured in a gas-burette, C, which likewise contains 100 c. c., and is divided into fifths of a cubic centimetre. The substance to be tested is dissolved in a 100 c. c. flask, the solution put into the burette B, and 50 c. c. of it run into

the flask A. Meanwhile the funnel-tube *a* is filled with the hypobromite solution and the pinch-cock *b* is opened, so that the liquid completely fills the lower part of the tube as well. By pouring water into D, after loosening the joint *c*, D and C are filled with water exactly to the mark for zero. Now the flask A is put to its cork, the joint at *c* is made again, and the apparatus is tried for tightness by running some water out of *d*; the level of the water in C will sink a little by the expansion of the air in A, but should become constant at once and remain so. Now by opening *b* a little hypobromite is run into A; the nitrogen is given off with effervescence and passes into C. From time to time a little water is run out of *d*, in order to prevent it from running over out of D. When the action slackens, more hypobromite is run in through the funnel till the liquid has reached the mark in the neck. Now all the nitrogen and, moreover, 50 c. c. of air have been forced over into C; to this must be added 0·3 c. c. for the air entering on attaching the india-rubber joint at *c*. The levels of the water in C and D are equalized, read off, and the volume of the nitrogen found by deducting 50·3 c. c. This volume must be reduced to 0° and 760 millimetres pressure by means of the formula

$$V_1 = \frac{Vb}{0{\cdot}76 \times (1 + 0{\cdot}003665\,t)},$$

in which *b* is the height of the barometer reduced to 0° and diminished by the tension of aqueous vapour for the temperature *t*.

Each cubic centimetre of nitrogen at 0° and 760 millimetres pressure corresponds to 0·0012566 gram nitrogen or 0·0015259 gram ammonia. It should not be overlooked that only half of the substance weighed off has been employed for the testing, which with some practice is finished in a few minutes.

The calculations for reducing the volume of gas to 0° C. and 760 millimetres pressure are saved or greatly simplified by the use of tables, of which we will mention those given by the author (in his 'Sulphuric Acid and Alkali,' Appendix to vol. iii.) and by Cl. Winkler ('Handbook of Technical Gas-Analysis,' translated by Geo. Lunge, p. 114 *et seq.*). In the work just mentioned I have also described, as an addition to Winkler's prescriptions, an apparatus constructed by myself which admits of the above correction without the use of a barometer and thermometer, and by a simple multiplication factor (p. 99). I have also

described there (p. 102 *et seq.*) an apparatus for carrying out Knop's method without his azotometer, viz. a "nitrometer" fitted with a "decomposition-flask." This apparatus is cheaper and more simply manipulated than the azotometer, while yielding quite as accurate results.

There is always some gas absorbed by the liquid contained in the decomposition-flask, and a correction must be applied on this account, according to the subjoined table, experimentally determined by E. Dietrich for the case in which 60 cub. centim. of liquid (50 of brominated soda and 10 of water) are used, of such strength that it is capable of liberating 200 cub. centim. of nitrogen. This table shows the number of c. c. to be added to the quantity found, when this quantity ranges from 1 to 100 c. c.

Correction for the Volume of Gas found by the Azotometer Method.

Found. c. c.	Add. c. c.	Found. c. c.	Add. c. c.	Found. c. c.	Add. c. c.	Found. c. c.	Add. c. c.	Found. c. c.	Add. c. c.
1	0·06	21	0·56	41	1·06	61	1·56	81	2·06
2	0·08	22	0·58	42	1·08	62	1·58	82	2·08
3	0·11	23	0·61	43	1·11	63	1·61	83	2·11
4	0·13	24	0·63	44	1·13	64	1·63	84	2·13
5	0·16	25	0·66	45	1·16	65	1·66	85	2·16
6	0·18	26	0·68	46	1·18	66	1·68	86	2·18
7	0·21	27	0·71	47	1·21	67	1·71	87	2·21
8	0·23	28	0·73	48	1·23	68	1·73	88	2·23
9	0·26	29	0·76	49	1·26	69	1·76	89	2·26
10	0·28	30	0·78	50	1·28	70	1·78	90	2·28
11	0·31	31	0·81	51	1·31	71	1·81	91	2·31
12	0·33	32	0·83	52	1·33	72	1·83	92	2·33
13	0·36	33	0·86	53	1·36	73	1·86	93	2·36
14	0·38	34	0·88	54	1·38	74	1·88	94	2·38
15	0·41	35	0·91	55	1·41	75	1·91	95	2·41
16	0·43	36	0·93	56	1·43	76	1·93	96	2·43
17	0·46	37	0·96	57	1·46	77	1·96	97	2·46
18	0·48	38	0·98	58	1·48	78	1·98	98	2·48
19	0·51	39	1·01	59	1·51	79	2·01	99	2·51
20	0·53	40	1·03	60	1·53	80	2·03	100	2·53

ADDENDA.

Page 4. *Value of the by-products of gas-making.*—Since the text was written, a great and beneficial change has taken place in this respect, and the value of coal-tar and the products obtainable therefrom has risen to a very great extent. It may now (July 1887) be taken as follows:—

	£	s.	d.	
Coal-tar (at the works)		15	0	per ton.
Benzol, 90-per-cent.		3	6	per gallon.
Benzol, 50-per-cent.		2	8	„ „
Crude naphtha, 30-per-cent. at 120°		1	2	„ „
Carbolic acid, crystallized 35°			11½	per lb.
Ditto, crude 60-per-cent.		2	9	per gallon.
Creosote, ordinary			1	„ „
Ditto, filtered for the Lucigen light.			1½	„ „
Grease oils, 22° Tw.	1	7	6	per ton.
Pitch, f. o. b. Liverpool		13	6	„ „
Anthracene 30-per-cent., per unit		1	0	
Ammonia, sulphate of (grey)	12	15	0	per ton.

P. 14. *Quantity of coal-tar produced and consumed in the United Kingdom.*—Lewis T. Wright (Journ. Soc. Chem. Ind. 1886, p. 559) estimates the production of tar in 1885 as 105,625,000 gallons, or 558,780 tons weight, of which about 7½ per cent. is used direct in the raw condition for tarring, asphalting, and other purposes, and not much exceeding 1 per cent. for retort-firing, so that the quantity going into the distiller's hands is 97,175,000 gallons.

Pp. 17 & 25. *Influence of the degree of heat and of the different kinds of coals on the quantity of tar produced.*—L. T. Wright (see above) states that as the distillation-temperature is increased the tar decreases slightly in quantity, but increases in specific gravity. Above a certain temperature, which differs for each kind of coal, the trouble caused by thick tar stopping up pipes &c. prevents the gas-making process from being carried on. In the average of gas-works the distillation-temperature is as high as can be conveniently attained with the present form of gas-making plant, so that there is practically no margin for any reduction in the output of tar by the employment of higher "heats."

The following table serves to illustrate the variations in the volume and weight of tar (and gas) yielded by coals distilled at widely different temperatures. The experiments were conducted in clay retorts with the ordinary form of gas-plant. The expression "normal temperature" means the highest practically and continuously possible in a modern gas-works. By "very high temperature" is meant one only practicable by careful nursing and for a short period.

Description of Coal.	Temp. of distillation.	Cubic ft. of gas per ton.	Gallons of tar per ton.	Spec. gr. of tar.	Tar per ton, lbs.	Weight per cent. on coals.
Derbyshire Black Shale No. 1	very high	11,128	10·63	1·210	128·62	5·74
,, ,,	normal	10,400	.....	1·185		
,, ,,	very low	7,856	11·50	1·145	131·67	5·88
Derbyshire Black Shale No. 2	very high	11,190	12·01	1·207	144·96	6·47
,, ,,	normal	10,400	.....	1·185		
,, ,,	very low	7,562	14·38	1·136	163·35	7·29
Notts Top Hard Cannel	normal	9,852	21·32	1 147	244·54	10·92
,, ,,	very low	7,125	23·81	1·116	265·72	11·86

P. 22. *Paraffin in coal-tar.*—Dr. Krämer (priv. comm.) regards the opinion that solid paraffin occurs in real coal-tar as erroneous. In his opinion, solid paraffin only appears whenever cannel coal, or shale, or similar substances have been employed along with real coal; and the reason why naphthalene and paraffins generally occur together is simply this, that coals yielding much naphthalene usually require an addition of the above-mentioned substances in order to produce good gas. [It should be noticed that Dr.

Ronald's experience of 20 years was made with Scotch cannel coals.]

P. 32. *Benzenoid hydrocarbons from the tar obtained in making Pintsch-gas.*—According to Krämer (priv. comm.) it is easy to separate these from the olefins by means of free chlorine, which fixes the latter, so that benzol &c. can be blown off. This process has been carried out in practice; but it is now supplanted by a still better one, which cannot as yet be divulged.

P. 39. *Quantity of coal distilled in coke-ovens.*—According to official returns, 5,106,696 short tons (=4,559,455 tons of 2240 lbs.) of coke were produced in coke-ovens in the United States during the year 1885; 78 per cent. of this quantity referring to Pennsylvania. It would appear that so far none of this has been utilized for obtaining tar and ammonia. Nearly the whole of it was made in beehive-ovens of the ordinary kind.

P. 48. *Adapting beehive coke-ovens to the recovery of by-products.*—This problem seems to have approached a better solution by entirely doing away with the old method of coking by partial combustion of the coal, and applying all the heat from without, by means of bottom-flues; the necessary degree of heat being attained by a previous heating of the combustion-air in Siemens's or other "recuperators." This is done in the ovens patented by C. Otto and Co., and the Hibernia and Shamrock Coal Company, and erected at the Shamrock pit in Westphalia in 1886 (G. P. 37280). There are two recuperators arranged alongside in the wall, between two sets of coke-ovens. One of these stores up the heat of the fire-gases passing through it, while the other yields the heat, received before, to the air which is to maintain the combustion of the residual gases in the bottom flues. Once an hour the direction of the draughts is changed, so that the two recuperators mutually exchange their mode of working. The gases given off in the coking-chambers are drawn off by a pump, and forced back into the flues below the soles of the ovens. Between the escape-pipe, which is situated in the crown of the oven, and the pump, there is an hydraulic main, and the usual condensing and scrubbing arrangements, just as constructed for the Coppée-Otto ovens (p. 50 *et seq.*). At the Shamrock pit each oven carries a charge of 4 tons, and gets through it within 55 hours; the yield is 80 per cent. of large-sized coke (against 65 to 68 per cent. got by the old process), 5 or 6 per cent. of tar, and 1 per cent. of sulphate of

ammonia; also 244 cubic metres (say 8540 cubic feet) of gas per ton of coal. The quality of the coke is altogether as good as that of the ordinary beehive coke; the reason why this is the case, in spite of the heat being exclusively communicated by means of bottom flues, probably arises from the fact that the coal is spread in a comparatively shallow layer on the oven-sole, and the very large increase of yield is hence an entire gain. Apart from that, the time of coking the charges is very much reduced, and there are, moreover, the by-products.

From inquiries made in a reliable direction, it appears that the object of the above-described invention is solely that of utilizing existing beehive-ovens in a better manner, by adapting them to the new system (which is a rather expensive process); but nobody would think of building ovens of this kind apart from the tar question, for the simple reason that the discharging of beehive-ovens is infinitely more troublesome than that of horizontal coke-ovens. Nobody in Westphalia seems to doubt that the latter are the best coke-ovens, and that beehive-ovens will go out altogether.

An analysis of the tar obtained in beehive-ovens modified on the system described in the above-mentioned German Patent No. 37280, was made at the laboratory of the Bochum mining-school, and yielded the following results:—

Spec. gravity at 19°, 1·106.
1 kilo yielded up to 160°:—20 c. c. water.
47 c. c. light oil.
1 kilo yielded up to 240°:—188 c. c. middle oil.

The light oil contained 5 per cent. acid oils, and yielded at:—

	95°-100°	110°	120°	130°	140°	150°	160°	170°	180°	190°
per cent.	2	4	12	24	38	51	64	74	80	87

The middle oil contained 24 per cent. acid oils, but very little naphthalene, and yielded at:—

	182°-190°	200°	210°	220°	230°	240°
per cent....	5	18	42	62	76	85

There was only 2·63 per cent. fixed carbon, against about 10 per cent. in other coke-tars, and about 20 per cent. in gas-tar.

The light oil was, unfortunately, tested only qualitatively for benzol, but it is said to be worked up advantageously by tar-distillers. Another analysis, made in my own laboratory, will be quoted lower down, in connection with the "Germania" tar.

New coke-ovens with recovery of by-products have been patented by Röchling (G. P. 38312) and J. Collin (36518).

P. 59. *Composition of coke-oven tars.*—I have recently been supplied with large samples of tar—1st, from the "Germania" coke-ovens built on the Hoffmann-Otto principle, exactly as described in the text; 2nd, from the modified coke-ovens, built according to the German patent 37280 (comp. p. 711), at the "Hibernia und Shamrock" pit near Bochum (Westphalia). The analysis was performed by myself, in company with Dr. Jac. Schmid, and yielded the following results:—

	A. "Germania" tar.	B. "Hibernia" tar.
Spec. grav. at 15°	1·1198	1·1368
Light oil up to 170°	6·55 p. c. weight = 7·43 p. c. vol.	4·88 p. c. weight = 5·24 p. c. vol.
Middle oil up to 230°	10·54 p. c. weight = 10·16 p. c. vol.	14·14 p. c. weight = 13·97 p. c. vol.
Creosote oil up to 270°	7·62 p. c. weight = 7·23 p. c. vol.	9·99 p. c. weight = 9·77 p. c. vol.
Anthracene oil	44·35 p. c. weight.	22·65 p. c. weight.
Pitch	30·55 p. c. weight.	43·41 p. c. weight.
Water	trace.	3·84 „ „
Loss	0·39 p. c. weight.	1·09 p. c. weight.
	100·00	100·00

	"Germania" tar.	"Hibernia" tar.
Light Oil:		
Loss by chemical washing	18·42 p. c. vol.	33·05 p. c. vol.
(including phenols)	(3·80 „ „)	(5·32 „ „)
Distillate between 78 and 100°	8·11 „ „	24·39 „ „
„ „ 100 and 140°	17·56 „ „	
Spec. grav. of joint distillate at 15°	0·869 „ „	0·862 „ „
Residue beyond 140°	55·91 „ „	42·56 „ „
Middle Oil:		
Phenols (crude)	26·0 „ „	37·66 „ „
Naphthalene (crude)	43·30 „ weight.	7·76 „ weight.
Creosote Oil: Phenols	11·0 „ vol.	18·33 „ vol.
Naphthalene (crude)	43·6 „ weight.	4·43 „ weight.
Anthracene Oil yielded crude anthracene, percentage on tar	4·13	0·93
containing pure anthracene	12·90	25·67
Pitch. Softening-point	165°	160°
Containing fixed carbon	51·56 p. c.	42·44 p. c.

The *distillate from the washed light oil* up to 140° could be nitrated without leaving any residue, and yielded 133 per cent. weight of nitro-compounds of spec. grav. 1·191, yielding only 1·1 per cent. up to 190°. It can therefore be regarded as consisting entirely of "aniline-benzol," in which certainly a good deal of xylene in comprised. The portion boiling above 140° contained a considerable proportion of naphthalene; but as this would be compensated by some naphtha, returned in the working of the middle oil, the whole of that portion may be called "heavy naphtha," without leading to the expectation that all of it can be obtained in the state of commercial "solvent naphtha."

On rectifying the washed light oil from the "Hibernia" tar, the thermometer rose rapidly above 100°, then slowly to 140°. A considerable portion distils only above 170°. In the nitrification test there was obtained 129·6 per cent. weight of nitro-compounds, spec. grav. 1·188. On distilling them there escaped, between 110° and 190°, 2·47 per cent. of an oil which resisted further nitrification. Hence this "aniline-benzol" is not as pure as that from the Germania tar, and it evidently contains, moreover, very little benzene, but chiefly toluene and xylene. Its value is therefore much less than that of the benzol from the Germania tar. From the above results we can now deduce the following table of the products to be recovered from those two tars:—

	A. "Germania" tar.		B. "Hibernia" tar.	
Aniline-benzol	.....	1·68	.....	1·12
Heavy naphtha	.....	3·64	.....	2·06
Crude naphthalene from middle oil	4·54	.....	1·09	
" " " creosote oil	3·15	.....	0·44	
" " " total	.....	7·69	.....	1·53
Crude phenols from light oil	0·25	.....	0·28	
" " " middle oil	1·56	.....	4·90	
" " " creosote oil	0·42	.....	1·75	
" " " total	.....	2·23	.....	6·93
Anthracene, calculated as commercial 33 per cent.	.....	1·59	.....	0·72
Creosote oil = middle oil + creosote, minus phenols and naphthalene	.....	8·24	.....	15·67
Anthracene oil filtered	.....	42·76	.....	21·93
Pitch (very hard)	.....	30·55	.....	43·41
Water	.....	.....	.....	3·84
		98·38		97·21

Of course these results will not exactly correspond to those obtainable on the large scale, but they allow of drawing the following inferences :—

Closed coke-ovens of the modified Coppée type (Hoffmann-Otto's system) yield a description of tar at least equal in value to ordinary gas-tar. The "benzol" contains a good proportion of real benzene, and is practically free from non-nitrifiable products. There is a good deal of heavy naphtha. The quantities of phenol, naphthalene, and anthracene are normal. Unlike gas-tar, there is much less creosote oil and hard pitch than anthracene oil, which is rather an advantage than otherwise. All this is easily understood, since those ovens work at least at the same heat as gas-retorts.

Ovens of the beehive class, modified by applying to them *external* heating-flues and recuperators, which work at a lower temperature than those just mentioned, yield a somewhat inferior tar. The "benzol" contains very little benzene, and a notable proportion of non-nitrifiable products. There is also less naphtha and much less anthracene. Moreover it is very difficult to dehydrate. The very small proportion of naphthalene and the large proportion of phenols it contains is very noteworthy. Still this tar must be classed with gas-tar and worked up in the same way; it is entirely distinct from other tars, obtained from internally heated beehive coke-ovens of the Jameson type (p. 46).

P. 89. *Schulze's theory of the formation of benzenoid hydrocarbons from phenols.*—In the opinion of Dr. Krämer this theory has no foundation, since the phenols are much more stable than the olefins or even the benzenes. The latter are probably formed from the paraffins through the intermediary stage of olefins. If any oxygenized substances cooperate, they belong to the class of fatty acids, lactones &c., or else they are semi-phenols, *i. e.* phenols with long lateral chains, such as occur in brown-coal and gas-producer tars.

P. 92. *Benzene from naphthenes, &c.*—Dr. Krämer believes that these naphthenes pass over into benzenes with greater difficulty than the olefins, and regards the latter also merely as a transitional stage from the paraffins, which, according to him, must be looked at as the "matière première." That phenols are practically absent from petroleum gas-tar follows from their extremely slight proportion in the crude petroleum itself. Dr. Krämer has found

American petroleum-residues to yield even more benzenoid hydrocarbons than Caucasian ones (comp. p. 93).

P. 109. *Naphthenes.*—Krämer and Böttcher* confirm and greatly extend the observations formerly made upon the presence in petroleum of hydrogen-addition products of the benzene series, which they believe to be identical with Markownikoff's "naphthenes," retaining the latter name for those compounds which are very distinct from the olefins, but isomeric with them; they principally differ from the olefins by not combining directly with bromine and not dissolving in concentrated sulphuric acid. Krämer and Böttcher assume these naphthenes to occur in coal-tar oils as well, along with real paraffins. New observations by Markownikoff and Spady † decidedly confirm the assumption that the "naphthenes" are hydrogen-addition products of the aromatic series, and this question seems to be settled now.

P. 111, footnote ‡. *Occurrence of benzene &c. in petroleum.*—Krämer and Böttcher (Berichte, 1887, p. 601) have completely confirmed Markownikoff's results, according to which benzene, toluene, xylene, &c. are present in large quantities in petroleum. The opinion expressed by me on p. 111, that much of the aromatic hydrocarbons found after passing petroleum through red-hot tubes may have been already pre-existent in the original substance, is thereby naturally strengthened.

P. 121.—*For separating ethyl-benzene from the three isomeric xylenes,* Friedel and Crafts (Compt. rend. ci. p. 1218) describe a method, founded upon the unequal solubilities of the bromides in petroleum spirit. This process is too complicated for technical purposes.

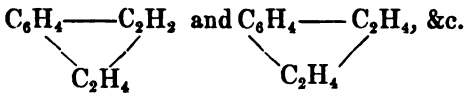
P. 122. *Trimethyl-benzenes and Tetramethyl-benzenes.*—K. E. Schulze § finds that the principally occurring trimethyl-benzene is mesitylene (position 1, 3, 5); the 1, 3, 4 and 1, 2, 3 isomers occur in smaller quantities.

Of the tetramethyl-benzenes the 1, 2, 3, 5 isomer is prevalent; the 1, 2, 4, 5 occurs in smaller quantity.

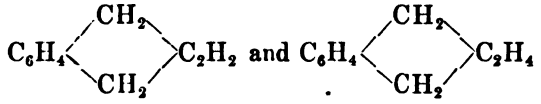
P. 125. *Naphthalene hydrides, &c.*—Krämer and Böttcher‖ believe these compounds to be identical with those contained in petroleum, and boiling at the same temperatures. They do not

* Berichte, 1887, p. 595.
† Ibid. p. 1850.
§ Ibid. p. 410.
‖ Ibid. p. 603.

believe them to be real naphthalene hydrides, because their chemical behaviour does not correspond with this assumption, but perhaps to have the constitutional formula:



This would explain why they do not add bromine (owing to the presence of a closed chain), and why they yet possess the property of forming sulphonic acids (owing to the presence of acetylene groups), whilst they do not pass into naphthalene by over-heating. The real hydrides of naphthalene, as expressed by the formulæ:



would do the latter. The compounds, possessing the formulæ $C_{11}H_{14}$, $C_{11}H_{12}$, $C_{12}H_{14}$, &c., found by Markownikoff in Caucasian petroleum (comp. p. 111, footnote), evidently belong to this series. Krämer and Böttcher have found them both in petroleum and in coal-tar.

P. 132. *Phenanthrene.*—Dr. Krämer has found the boiling-point of pure phenanthrene obtained from the picrate = 320–322° (Gräbe formerly found 325–330°).

P. 133. *Pyrene.*—Bamberger and Philip* discuss the constitution of this hydrocarbon, and show that it consists of a naphthalene nucleus, with two benzene nuclei inserted above and below.

P. 137. *Methyl-ethyl-ketone* has been found in fore-runnings from benzol-distilling treated with dilute sulphuric acid, along with acetone, by K. E. Schulze (Berichte, 1887, p. 411). He believes them to have been formed from methyl- and ethyl-acetylene by the action of the acid.

P. 142. *Proportion of the isomeric cresols in coal-tar.*—K. E. Schulze† estimates the ordinary cresol to consist of about 40 per cent. metacresol, 35 per cent. orthocresol, and 25 per cent. paracresol.

* Ber. d. deutsch. chem. Ges. 1887, p. 365.

† Berichte, 1887, p. 410.

P. 145. *Xenols in coal-tar.*—Schulze (*eod. loco*) finds that the 1, 3, 5 xenol forms the principal portion of coal-tar xenols; the 1, 2, 4 xenol is present in smaller quantities.

P. 151. *Properties of aniline.*—The specific gravity at 15° is =1·0270. 100 parts of water dissolve 3 of aniline in the cold, or 6 of aniline hot.

P. 152. *Pyridine.*—In lieu of antipyrine, kairine and thalline ought to be mentioned as pyridine derivatives; antipyrine has been recognized as not belonging to this class. The stability of the pyridine nucleus against oxidizing agents does not, of course, extend to the lateral chains. Hoffmann has established a group-reaction for pyridines, viz. the peculiar strong smell produced on heating these bases with methyl-iodide and potassium hydrate. The pyridene hydrate mentioned in the text has not been found in coal-tar directly, but in the mixture of bases isolated from vitriol-tar, where it may have been formed during the treatment.

P. 153. *Picoline.*—The γ picoline [γ pyridine, line 8, is a clerical error], only supposed to be present by Goldschmidt and Constam, has been proved to exist in coal-tar by K. E. Schulze*.

Lutidines.—The research alluded to in the text has been since published †. A little later K. E. Schulze ‡ has confirmed the presence of *aa* and *aγ* lutidine.

Collidine.—The properties mentioned in the text are those of a collidine obtained from bone-tar. There are a great many isomeric collidines known now, but it is quite uncertain which of these occur in coal-tar.

P. 155. *Process for preparing the bases from coal-tar.*—Dr. Krämer points out that this is done most advantageously by the process described in the German patents Nos. 34947 and 36372, mentioned on p. 445. The bases obtained in this way can be separated on the large scale by a rectifying-column.

P. 159. *Free carbon.*—Dr. Krämer reverts to the old opinion that the free carbon in coal-tar is principally due to decomposition of hydrocarbons at the highly-heated sides of the retort; only a slight proportion might be due to mechanically carried-over coke-dust.

P. 187. *Burning tar as fuel.*—L. T. Wright § gives a more

* Berichte, 1887, p. 413. † *Loc. cit.* p. 127. ‡ *Loc. cit.* p. 413.
§ Journ. Soc. Chem. Ind. 1887, p. 36.

detailed account of his experiments on generating steam by means of tar and creosote oil, injected by steam, as compared with various descriptions of coal and coke. The trials altogether extended over 46 days, and the results were as follows :—

	Actual evaporation, lbs. of steam per lb. of the fuel.	Theoretical evaporation, calculated from the composition of the fuel.	Percentage of real or theoretical evaporation.
Nottingham top hard Cannel.	8·78	12·27	71·56
Yorkshire Silkstone coal	10·01	14·24	70·30
Top hard Cannel coke	9·91	12·23	81·03
Silkstone gas-coke	11·15	13·83	80·62
Tar, injected by steam	12·71	15·06	84·40
Creosote oil, ditto.....	13·35	16·78	79·56

Afterwards he abandoned the injection by steam in favour of a very simple system, described in the text, which causes the tar to run in between two fire-tiles; the lid carsobon is deposited behind on a grate as a kind of coke or breeze, and is burned there. The labour is very light, and there is only 0·08 inch vacuum required for draught against 0·25 inch with an ordinary coke-fire. The chimney gases tested, on an average, 12·9 per cent. CO_2, when no smoke was produced.

L. Körting* likewise objects to the common statement that 1 part of tar goes as far as 2 parts of coke. The comparison might hold good for the very imperfect systems of coke-firing formerly in use, but it is very different with the excellent gas-producers now employed for heating gas-retorts. At Munich, for instance, they require only 9·6 kilog. of coke for distilling 100 kilog. of Saar coal, or 12 kilog. for 100 of Westphalian coal. Theoretically, that is calculating the heating-value of both tar and coke by Dulong's formula [which is certainly very incorrect !], in the ratio of 8660 against 7270 heat-units per kilog., the above quantities of coke ought to be replaced by 8 and 10 kilog. of tar respectivly. This is, however, less than Körting was ever able to manage, although it is said to be done at Vienna. One of the difficulties to contend with is: that the supply of air cannot, with tar as fuel, be kept close to the theoretical limit, as is possible in gas-producers, for in the case of tar this would

* Journal für Gasbeleuchtung, 1886, p. 543.

frequently lead to producing black smoke. Nor is it possible to employ previously-heated air, for in this case the tar-supply pipe must have all air-tight joints in the fire-door, so that its end cannot be directly observed; and whenever any irregularities occur in the supply of tar, twice the quantity may be burned than is necessary with a perfectly regulated supply. Of all the methods employed for tar-firing, Körting prefers atomizing by steam, but not with the atomizers universally employed in England, but with those made by Körting Brothers (p. 184). With these he reduced the consumption of tar in a six-retort furnace from 20 to 13·5 kilog., and in an eight-retort Liegel furnace, which had formerly consumed 12 kilog. of coke, to 11 kilog. of tar per 100 kilog. of coal, distilling 6800 kilog. in 24 hours.

Böhm in Stuttgart injects 200 kilog. tar into 480 kilog. coke for heating a seven-retort furnace during 24 hours; this represents 15 to 16 parts of fuel to 100 of coal distilled.

J. Key* states that no compressed air or steam is necessary, but that tar can be burned by gravitation-feeding when previously filtered.

W. Horn (G. P. 36403) attaches to the fire-door a box containing a special contrivance for running-in tar, so that the fire can be maintained either by ordinary or by liquid fuel.

Westphal's naphtha-burner† for forge-fires causes the liquid fuel to issue from a number of annular openings; it is atomized by compressed air, and, after lighting, the flame is directed by a special kind of nozzle upon the object to be heated. This burner is said to effect its purpose very well with petroleum residues; it would seem to be less adapted for coal-tar, which would clog it up too easily, but it might do very well for creosote oil.

F. Mörth (B. P. 4135, 1886) introduces a mixture of superheated fuel and hydrocarbon underneath the fire-grate by a series of horizontal tubes perforated on the top.

Tarbutt's patents (B. P. 14269, 1883; 5599, 1886) employ compressed and highly superheated air for atomizing the liquid fuel. It is claimed for this process, which has been very successfully applied to steamboat fires, that for this purpose it is very superior to the atomizing by steam, because in the latter case there is

* Engineering, 1886, p. 450.

† Dingler's Polytech. Journal, vol. cclxiii. p. 373.

a great waste of water which has to be made up by pumping sea-water, and thus concentrating the salts within the boiler; while in the former case the steam is employed for compressing air, and is condensed to distilled water by surface-condensers.

Burning tar as a motive power, in a way similar to Ericson's caloric engine, is the object of an invention by James Hargreaves. According to experiments described in the 'Chemical Trade Journal,' June 11, 1887, an engine with a working cylinder of 25 in. diameter and 18 in. stroke yielded an indicated horse-power of 29·7, with a consumption of 2 gallons of tar per hour. The efficiency is 0·174, that is, about the same as that of the best gas-engines or steam-engines; but in lieu of 1000 cubic feet of gas, of a value of three shillings in many places, only 3 gallons of tar, worth three pence, is used. It is needless to say that this invention, if found to be successful in the long run, will be of immense service to gas-works in keeping up the value of tar.

P. 217. *Condensing-worms.*—Some German tar-works use cast-iron worms as well as wrought iron (Dr. Krämer).

P. 229. *Receivers.*—In Germany some even of the larger tar-works have separate receivers for each tar-still (Dr. Krämer).

P. 230. *Advantage of a vacuum in the separation of the fractions in distillation.*—The assumption that the lowering of boiling-points, caused by employing a partial vacuum, facilitates the separation of the various fractions, has been refuted by more recent investigations. The differences remain practically the same.

P. 234. *Percentage of carbolic acid in crude phenol.*—Dr. Krämer considers it impossible that any crude phenol should contain anything like 65 per cent. of carbolic acid. Probably the product spoken of in the text as "crystallizable" was still very impure.

P. 290. *Anthracene in pitch.*—Good hard pitch contains only traces of anthracene (Dr. Krämer). This quite coincides with the small proportion of anthracene found in pitch by Mr. Watson Smith, and seems to show that all previous hopes in this direction were not founded on any real basis.

Pp. 306 & 309. *Purification of anthracene.*—Remy and Erhart (G. P. 38417) dissolve 100 parts of rough anthracene in 150 of oleic acid, previously heated to 110° or 120° C., with stirring, and allow the mixture to cool, whereupon anthracene crystallizes out

with comparatively few impurities. The oily solution is removed by filtering, centrifugal force, and pressing, and the last traces of oil are got rid of by saponification with alkali, or by washing with petroleum or similar solvents. The purified anthracene remains as a yellowish or greenish-white powder.

P. 309. *Anthracene oil, drained from rough anthracene,* is sometimes mixed with sulphate of copper or chloride of zinc, and with a certain quantity of rosin or boiled linseed-oil. In this state it is sold under the name of "carbolineum," and recommended very strongly for painting timber, such as railway-sleepers, harbour-piers, telegraph-poles, fences, wood floors, &c. It is stated to be much preferable to painting with tar (which is very likely); but it seems very doubtful whether it will answer as well as properly injecting under pressure, as described p. 348 *et seq.*

P. 329. *Substances occurring in creosote oil.*—To those enumerated in the text we must probably add tetramethylbenzenes (Schulze), and undoubtedly bodies belonging to the class of "naphthenes" (Krämer and Böttcher, comp. Addendum to p. 109, *ante*).

P. 374. *Neutral oils, forming the bulk of the "carbolic oil"* (boiling between 170° and 210°).—According to K. E. Schulze * these oils contain about 50 per cent. oils resinifiable by sulphuric or hydrochloric acid, 15 per cent. trimethylbenzenes, 15 to 20 per cent. tetramethylbenzenes, and 15 to 20 per cent. naphthalene; also a paraffin melting at 20°.

Pp. 382, 386. *Reddening of carbolic acid.*—E. Mylius (Chemische Industrie, 1887, p. 146) has noticed that the same sample of carbolic acid, after having been liquefied by water, will keep its colour in one bottle, but will turn red in another. This behaviour is evidently connected with the quality of the glass. It was found that traces of potassium hydrate or carbonate or of ammonia caused a discoloration, but ferric or zinc hydrate had no effect; and a trace of hydrochloric acid prevented the discoloration in a bottle which had previously stained the carbolic acid. This explanation does not, however, fit all cases; there are samples of carbolic acid which turn red in any case.

* Ber. d. chem. Ges. 1887, p. 409.

In order to decolorize red carbolic acid, S. Demant (Chemiker Zeitung, 1887, Rep. p. 78) liquefies it in the water-bath, adds 11 parts of alcohol to 89 parts of carbolic acid, and exposes the mixture to freezing. When most of it has solidified, the liquor is drained off the crystals, which are then colourless.

P. 392. *Phenol in German tars.*—These yield only about 0·5 per cent. of phenol (Dr. Krämer).

P. 416. *Moulding of naphthalene.*—A special machine for this purpose has been constructed by Neujean (G. P. 36708).

P. 475. *Chemically pure benzene.*—Willgerodt (Journ. prakt. Chem. xxxiii. p. 479) recommends purifying benzene from thiophen by agitating with chlorine-water.

P. 481. *Substances contained in the "fore-runnings" of benzol-stills.*—In addition to those mentioned in the text, K. E. Schulze has found methylic cyanide, acetone, and methyl-ethyl-ketone. The ketones may have been formed during the acid-treatment, and do not seem to pre-exist in the tar (Berichte, 1887, p. 411).

P. 542. *Percentage of nitrogen in coal.*—A very important research on this subject and on the production of ammonia from coal has been carried out by E. Schilling, and published in his Inaugural Dissertation, Munich, 1887. The following statements are taken from that pamphlet.

All former observers * have estimated the nitrogen in coal (and coke) either by Dumas's method or by combustion with soda-lime. Already Forster had pointed out the inaccuracies of these methods, but his own modifications do not yield more accurate results. These are, however, to be obtained by Kjeldahl's method, which was only introduced in 1883, but which has already supplanted all the other methods for testing manures &c. It is also far superior to the other methods in estimating the nitrogen in coal and coke. By this method † Schilling found the following percentages of nitrogen :—

* To those mentioned on p. 542 should be added Knublauch, who found in five descriptions of Westphalian coal from 1·215 to 1·612 per cent., and in two descriptions of English coal 1·102 and 1·443 per cent. of nitrogen.

† Which is also strongly recommended by S. Schmitz, Stahl u. Eisen, 1886, p. 47.

	Single Experiments.	Average.
Westphalian coal ("Consolidation")	1·50–1·49	1·50
Saar Coal ("Heinitz I.")	1·09–1·02	1·06
Silesian coal ("König in Luise")	1·38–1·35	1·37
Bohemian coal (from Littiz)	1·38–1·34	1·36
Saxon coal ("Bürgergewerkschaft") ...	1·25–1·15	1·20
English coal (Boldon gas-coal)	1·49–1·40	1·45
Bohemian cannel-coal (Plattenkohle) ...	1·51–1·46	1·49
Bohemian brown-coal (Falkenau)	0·56–0·48	0·52

On the whole, it was found that the percentage of nitrogen in the various descriptions of coal was in inverse proportion to the percentage of oxygen.

P. 516. *Yield of ammonia from coal.*—Knublauch * found, in three cases, that 31 to 36 per cent. of the nitrogen contained in the coal remained behind in the coke. Of the total nitrogen contained in five descriptions of Westphalian coal only from 10·7 to 13·7 per cent. was recovered in the shape of ammonia; of two English coals 9·39 to 24·34 [?] per cent. He estimates that of 100 parts of nitrogen there is recovered—

In the coke	31	to	36	parts.
As ammonia	10	„	14	„
As ferrocyanide in the spent oxide	1·5	„	2	„
In the tar	1·0	„	1·3	„

leaving about 50 parts of elementary nitrogen in the coal-gas.

Guéguen and Parent † do not give any useful information on this subject.

E. Schilling (comp. above) found the percentage of nitrogen in real coal = 1·22 to 1·39, in Bohemian Plattenkohle = 1·00, in brown-coal = 0·58, but with this should be combined the yield of coke, which varied from 40·5 to 74·2 per cent. of the coal; and we thus get the following tables concerning the distribution of the nitrogen of coal:—

* Journ. für Gasbeleuchtung, 1883, p. 440.

† Etude sur l'utilisation pratique de l'azote des houilles &c. Paris, 1885 (J. Michelet).

Nitrogen.	West-phalian.	English (Boldon)	Silesian.	Bohe-mian.	Saxon.	Saar.	Bohem. Cannel.	Bohem. Brown-coal.
I. 100 parts of coal contained :—								
Total	1·50	1·45	1·37	1·36	1·20	1·06	1·49	0·52
Left in coke	0·96	1·02	0·95	0·77	0·86	0·85	0·56	0·23
Volatilized	0·54	0·43	0·42	0·59	0·34	0·21	0·93	0·29
II. 100 parts of nitrogen reappeared :—								
In the coke	80	72	70	69	64	57	44	38
Volatilized	20	28	30	31	36	43	56	62

In order to test the actual yield of ammonia, E. Schilling made a large number of experiments at the Munich gas-works with a working retort specially fitted up for this purpose, but otherwise working under the normal conditions of gas-making and at a temperature of 1160° to 1220° C., as determined by Prinsep's alloys. He always made parallel experiments without and with addition of lime, employing 2½ per cent. of the coal (Cooper's process). The following table (p. 726) embodies his results.

This table most clearly shows that the coal containing most nitrogen did not necessarily yield the highest proportion of ammonia; that even in real coal the proportion of nitrogen recovered in the shape of ammonia may vary from 6·4 to 17·4 of 100 total nitrogen, that is almost as 1 : 3; and that "liming" the coal has, in some cases, a very slight effect, and may even cause a decrease of the quantity of NH_3; whilst in other cases its effect is very considerable, viz. an increase of 30·7 per cent. in the case of English (Boldon) and of Saxon coal. It stands to reason that among the infinite variety of English gas-coals the differences will be quite as pronounced.

By a special series of experiments on a working scale, Schilling completely disproved the statement of Guéguen and Parent (comp. above) that the increase of ammonia by "liming" is due to the water of hydration of the lime increasing the quantity of steam present in the retort; the contrary is decidedly the case.

Yield of Ammonia and Distribution of Nitrogen from various descriptions of Coal.

	Silesian.	Westphalian.	Bohemian.	English.	Saar.	Saxon.	Bohemian Cannel.	Brown-coal.
100 parts coal yielded parts of NH_3, without lime.	0·284	0·248	0·237	0·189	0·188	0·094	0·221	0·129
Ditto, with lime	0·298	0·276	0·227	0·247	0·209	0·173	0·229	0·126
Increase or decrease of NH_3 by liming, percent. of total NH_3.	+4·9	+11·3	−4·2	+30·7	+11·2	+84·4	+3·6	−2·3
Percentage of N given off as NH_3, without lime.	17·4	13·6	14·2	10·8	14·8	6·4	12·4	20·7
Ditto, with lime	17·9	15·2	13·8	14·0	16·2	11·9	12·7	19·9
Percentage of N left in coke (without lime).	69·0	64·0	57·0	70·0	80·0	72·0	38·0	44·0
Percentage of N as free N, cyanides and tar, without lime.	13·6	22·4	28·8	19·2	5·2	21·6	49·6	35·3
Ditto, with lime	13·1	20·8	29·2	16·3	3·8	16·1	49·3	36·1
Total N, percent. of coal	1·37	1·50	1·36	1·45	1·06	1·20	1·49	0·52
Of 100 parts volatile N there appears as NH_3, without lime.	56	46	33	36	74	23	20	37
Ditto, with lime	58	42	32	47	81	43	20	36

Schilling believes it probable that the greater or smaller proportion of the total nitrogen has some relation to the percentage of oxygen in the coal, those coals which contain less oxygen generally giving out more of their N as NH_3 than *vice versâ*. But this observation did not hold good in all cases, and would certainly require more extended investigations to be confirmed.

P. 647. *Grüneberg and Blum's ammonia-still.*—A modification of this still, in which the lime-vessel is made to surround the stepped cone, has been given up, because the lime burned fast on the sides of the vessel.

APPENDIX.

Tables I., II., III.

(for reducing the specific gravities of liquids lighter than water to the normal temperature of 15°·5 C.,=60° F.).

Note. The scale of reduction is not the same for high and low temperatures; hence three tables are given. When the observed temperature is *below* the normal, the figures in the table must be *deducted* from the observed specific gravity in order to reduce this to the normal temperature, and *vice versâ*.

I. For Specific Gravities from 0·880 downwards.

Degrees C.	2	4	6	8	10	12	13½	15½
Deduct ...	0·0105	0·009	0·008	0·006	0·0045	0·003	0·002	0

Degrees C.....	17½	19½	21½	23	25	27	29
Add	0·001	0·0025	0·004	0·0055	0·007	0·008	0·010

II. For Specific Gravities between 0·880 and 0·920.

Degrees C.	2	4	5½	7	9	10½	12	14
Dduct ...	0·010	0·0085	0·0075	0·0065	0·005	0·004	0·0025	0·001

Degrees C..	15½	17	19	20½	22	24	25½	27	29
Add	0	0·001	0·0025	0·0035	0·005	0·006	0·007	0·008	0·0095

III. For Specific Gravities between 0·920 and 0·960.

Degrees C.	1½	3	4½	6	7	8½	10	11½	13	14	15½
Deduct ...	0·010	0·009	0·008	0·007	0·006	0·005	0·004	0·003	0·002	0·001	0

Degrees C.	17	18	19½	21	22½	24	25	26½	28	29½
Add	0·001	0·002	0·003	0·004	0·005	0·006	0·007	0·008	0·009	0·010

Table IV.

(for comparing the degrees of Baumé, Cartier, and Beck with the corresponding specific gravities, for liquids lighter than water).

Degrees.	Baumé.	Cartier.	Beck.	Degrees.	Baumé.	Cartier.	Beck.
0	...	...	1·0000	17	0·952	0·955	0·9090
1	...	...	0·9941	18	0·946	0·948	0·9042
2	...	...	0·9883	19	0·940	0·941	0·8994
3	...	...	0·9826	20	0·933	0·934	0·8948
4	...	...	0 9770	21	0·927	0·928	0·8900
5	...	...	0·9714	22	0·921	0·921	0·8854
6	...	...	0·9659	23	0·915	0·914	0·8808
7	...	...	0·9604	24	0·909	0·908	0·8762
8	...	...	0·9550	25	0·903	0·901	0·8717
9	...	...	0·9497	26	0·898	0·995	0·8673
10	1·000	...	0·9444	27	0·892	0·889	0·8629
11	0·993	1·000	0·9392	28	0·886	0·883	0·8585
12	0·986	0·992	0·9340	29	0·881	0·877	0·8542
13	0·979	0·985	0·9289	30	0·875	0·871	0·8500
14	0·972	0·977	0·9239	31	0·870	0·865	0·8457
15	0·966	0·970	0·9189	32	0·864	0·859	0·8415
16	0·959	0·962	0·9139				

TABLE V.

(for comparing the Centigrade and Fahrenheit Thermometers).

C.	F.	C.	F.	C.	F.	C.	F.
+500	+932	+74	+165·2	+45	+113	+16	+60·8
400	752	73	163·4	44	111·2	15	59·0
300	572	72	161·6	43	109·4	14	57·2
200	392	71	159·8	42	107·6	13	55·4
100	212	70	158	41	105·8	12	53·6
99	210·2	69	156·2	40	104	11	51·8
98	208·4	68	154·4	39	102·2	10	50·0
97	206·6	67	152·6	38	100·4	9	48·2
96	204·8	66	150·8	37	98·6	8	46·4
95	203	65	149	36	96·8	7	44·6
94	201·2	64	147·2	35	95	6	42·8
93	199·4	63	145·4	34	93·2	5	41·0
92	197·6	62	143·6	33	91·4	4	39·2
91	195·8	61	141·8	32	89·6	3	37·4
90	194	60	140	31	87·8	2	35·6
89	192·2	59	138·2	30	86	1	33·8
88	190·4	58	136·4	29	84·2	0	32·0
87	188·6	57	134·6	28	82·4	−1	30·2
86	186·8	56	132·8	27	80·6	2	28·4
85	185	55	131	26	78·8	3	26·6
84	183·2	54	129·2	25	77·0	4	24·8
83	181·4	53	127·4	24	75·2	5	23·0
82	179·6	52	125·6	23	73·4	6	21·2
81	177·8	51	123·8	22	71·6	7	19·4
80	176	50	122	21	69·8	8	17·6
79	174·2	49	120·2	20	68·0	9	15·8
78	172·4	48	118·4	19	66·2	10	14·0
77	170·6	47	116·6	18	64·4	11	12·2
76	168·8	46	114·8	17	62·6	12	10·4
75	167						

All the temperatures mentioned in this book are in Centigrade degrees, but can be converted into Fahrenheit degrees by means of the above Table.

ERRATA.

Page 145, line 25, *for* 1866 *read* 1886.
„ 147, „ 20, *for* phenol *read* oxalic acid.
„ 152, „ 11, *for* one atom of C. *read* one CH-group.
„ 153, „ 8, *for* γ pyridine *read* γ picoline.
„ 201, „ 4 from the bottom, *for* 1880 *read* 1880 and 1886.

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